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WATER CHEMISTRY AND MICROBIAL CORROSION IN OILFIELD WATER HANDLING FACILITIES

FINAL REPORT

by:

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Part of Energy Mines and Resources
Cost-shared Energy Conversion Program
and Part of the Program of the Federal Panel
on Energy R&D [PERD]

April 30, 1992

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada.

DSS File No: 014SQ.23440-1-9062
DSS Contract Serial No: 23440-1-9062/01-SQ
CANMET Scientific Authority: Doug Gould

125 pp

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EXECUTIVE SUMMARY

This study was carried out in an oilfield waterflood operation in which produced brine is reinjected to displace more oil from the reservoir. Significant corrosion problems are associated with bacterial colonization of the water handling system. Previous work has focused on optimizing biocide treatment but there are limits to what is economically achievable by this approach.

This report describes results of an audit of chemical, biological and corrosion parameters measured across the Wainwright waterflood operation over a thirty month period. Based on the insights obtained and previous observation of shifts in microbial populations with variations in water chemistry, a series of runs was conducted in the field test facility at unit 13 waterplant to investigate the effect of specific chemical additions.

In the audit database, corrosion monitoring parameters generally failed to correlate with failure frequency or cost. Corrosion rate measurements by potentiodyne and weight loss coupons showed similar general trends but differed in absolute values. Optimization of corrosion control programs is hampered by the lack of a reliable way to predict corrosion failure in these systems.

Failure data did correlate with produced water salinity, hardness, suspended solids, oil and grease and soluble sulfate levels. Residual corrosion inhibitor did correlate with reduced failure as did residual sulfite from added oxygen scavenger. However, residual sulfite also corresponded to enhanced corrosion rates rendering its relationship to the failure data suspect. Addition of oxygen scavenger at the field test facility promoted sulfate reducing bacteria in the biofilm but did not alter the corrosion rate observed.

Corrosion inhibitor, oxygen scavenger and scaling inhibitor all showed evidence promoting bacterial growth suggesting that these additives may be providing nitrogen, phosphorus and sulfite/sulfate for microbial metabolism.

The bacterial population in Wainwright waterplants seems limited by the produced water salinity and pH. Correlation of the density of bacteria able to metabolize complex nutrients with suspended solids entering the system and inversely with the residual oxygen present suggests that these organisms may be breaking down complex organics like hydrocarbons to feed the anaerobic sulfate reducing bacteria in the biofilm population. These organisms can only use simple nutrients like acetate or lactate. Injection of these nutrients at the field test facility unit 13 caused increased growth of sulfate reducing bacteria confirming that these organisms are under organic limitation in Wainwright waterplants. Sulfate in these systems is limited by precipitation with excess barium but a dependence of sulfate reducing bacterial numbers on sulfate concentration was seen only for free water knock outs where sulfate is typically less than 1 mg/l.

Nitrate injection confirmed an inverse correlation between nitrate concentration and sulfate reducing bacteria, however, nitrate addition promoted biofouling by other organisms and led to much higher corrosion rates at the field test facility. This precludes use of nitrate as a control chemical in these water handling systems.

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A switch from turbulent to laminar flow had little impact on bacterial numbers but may have reduced their capacity for sulfate reduction.

The observation that injection of nutrients at the mg/l level can significantly shift the composition and corrosivity of biofilm populations suggests that it may be possible to adjust conditions to limit corrosion damage from microbially induced corrosion with or without the use of biocides.

The use of multi-variate statistics with the field audit information and consideration of the data on a unit by unit basis over the thirty month period may yield further insights into optimizing biocide performance in the Wainwright field.

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SOMMAIRE

Cette recherche concerne l'étude des eaux de pompage d'un bassin pétrolier où l'on exploite l'injection aqueuse pour améliorer l'extraction du pétrole. La saumure libérée de la phase organique de production étant réinjectée dans le puits. On a remarqué que la croissance de colonies bactériennes dans les eaux de pompage était étroitement liée aux problèmes de corrosion. Au cours d'une étude préliminaire, on a déterminé les conditions optimales d'utilisation de biocides, mais il s'est avéré que cette solution n'était pas économiquement rentable.

Ce rapport fait le bilan de travaux effectués dans un puits pilote de la région de Wainwright en Alberta. Au cours d'une période d'essais de plus de 30 mois, on a mesuré les facteurs chimiques, biologiques et corrosifs affectant le système de pompage. A la suite d'observations préliminaires faites sur les variations de la croissance microbienne en fonction des propriétés chimiques de l'eau, une campagne d'essais a été planifiée à l'unité de pompage No.13 du puits pilote, et l'on s'est proposé d'étudier l'action d'additifs chimiques dans les eaux de pompage.

Parmi tous les paramètres examinés affectant la corrosion, aucun n'a pu donner de corrélation directe avec la durée de résistance à la corrosion, ni le coût d'intervention. Les taux de corrosion mesurés simultanément par potentiodynométrie et par perte de poids de plaquettes-échantillons, ont produit une tendance relativement semblable, mais ont donné des valeurs absolues très différentes. L'étude des facteurs de corrosion a été entravée par le manque de moyen analytique fiable pouvant évaluer précisément le niveau de résistance à la corrosion.

La résistance à la corrosion est inversement proportionnelle au degré de salinité de l'eau, à sa dureté, à son taux de particules solides en suspension, à sa teneur en huile, en graisse et en sulfates solubles. Les inhibiteurs de corrosion résiduels, tels les sulfites des additifs d'absorption d'oxygène, améliorent la résistance à la corrosion. Cependant, certains sulfites résiduels ont aussi provoqué une accélération de la corrosion, ce qui rend leur interprétation assez douteuse. L'injection d'additifs d'absorption d'oxygène dans l'installation pilote a accru le taux de croissance des bactéries réductrices de sulfates dans le biofilm, mais n'a pas amélioré la résistance à la corrosion.

Les inhibiteurs de corrosion, les absorbants d'oxygène, et les inhibiteurs de dépôt calcaire, ont tous favorisé la croissance bactérienne. Il est possible que ces additifs fournissent l'azote, le phosphore, et les sulfites/sulfates nécessaires au métabolisme des microbes.

La croissance bactérienne dans les eaux de pompage du puits pilote de Wainwright est affectée par la salinité et le pH des eaux de retour. Le fait que la population bactérienne soit capable de métaboliser des nutriments complexes au sein des solides en suspension du système aqueux, malgré l'oxygène résiduel, suggère que ces micro-organismes décomposent aussi des produits organiques hydrocarbonés complexes, nourrissant ainsi la bactérie anaérobie et réductrice de sulfates dans la population du biofilm. Ces organismes ne pouvant métaboliser que des acétates ou des lactates. L'injection de ces substances au puits pilote de Wainwright a effectivement augmenté la croissance des bactéries réductrices de sulfates, ce qui confirme la "limitation organique bactérionutritive" des eaux de pompage du système de Wainwright. La concentration de sulfates solubles est faible à cause d'un taux important de baryum formant un précipité. Toutefois, l'effet de la dépendance des sulfates sur la croissance des bactéries réductrices de sulfates n'a été réellement observée que pour des eaux relativement "pures" où la concentration est généralement moins de 1 mg/L.

L'injection de nitrates a confirmé qu'une forte concentration de nitrates est inversement proportionnelle à la croissance de bactéries réductrices de sulfates. En outre, l'addition de nitrates a provoqué la croissance d'autres micro-organismes et a considérablement accéléré le taux de corrosion dans l'installation pilote. Ce résultat rejette l'emploi de nitrates comme agent de protection chimique contre la corrosion dans un tel système de pompage d'eau.

Le changement d'écoulement des eaux de pompage d'un régime turbulent en régime laminaire est demeuré insignifiant sur le taux de croissance bactérienne. On peut néanmoins supposer qu'un régime turbulent puisse ralentir la capacité des bactéries à réduire les sulfates.

On a observé que l'injection de substances bactérionutritives (au niveau du mg/L) pouvait considérablement changer la composition et la corrosivité des espèces microbiennes du biofilm. Cette observation permet d'ajuster les meilleures conditions pouvant limiter la corrosion générée par l'action microbienne, avec ou sans l'utilisation de biocides.

Les essais effectués dans ce puits pilote sur une période de plus de 30 mois, ont permis de faire des mesures en manipulant un grand nombre de variables. L'ensemble de ces données, en interprétant chacun des paramètres étudiés, offre statistiquement un large éventail de possibilités quant au problème de l'efficacité des biocides dans un champ pétrolifère, tel que celui de Wainwright.

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1.0 OBJECTIVES

- To develop a better understanding of how injection water chemistry influences the extent of microbial corrosion in oil field production facilities.

- Monitor *in situ* corrosion rates and correlate with injection water chemistry, and microbiological data.

2.0 INTRODUCTION

The control of biofilm development and related corrosion problems in oilfield water piping systems has been the aim of extensive and expensive effort in the oil industry for many years. Despite this effort, state of the art technology provides only a qualified level of risk assessment and control. Past projects in the NOVA HUSKY Field Test Facility have shown that even under selected biocide treatment using the best products available, fouling and microbial growth persist. Indeed levels below about 10^2 to $10^3/cm^2$ sulfate reducing bacteria seem unachievable within economic constraints. Further spontaneous shifts in microbial populations due to variations in chemical and other factors (Ferris, 1991, Jack *et al.* in press) can rival biocide effects in magnitude (Figure 1). A much better understanding of the microbial populations in the field and factors which influence them will be required before a significant improvement in practice can be achieved.

This report describes results of a field wide survey of chemical, biological and corrosion parameters gathered in the Wainwright waterflood operation of Husky Oil over a period of more than 30 months. An attempt has been made to divine parameters which are interrelated and to rationalize the correlations found.

Based on hypotheses developed in this process as well as correlations seen between microbial numbers and variations in water chemistry in a previous project (Ferris, 1991), a series of runs has been conducted in the field test facility. The results obtained relate to corrosion monitoring, conditions for microbial growth and the sensitivity of mixed populations to minor shifts in trace nutrient levels in water piping systems.

3.0 FIELD AUDIT

A database of chemical, corrosion and microbiological parameters over a thirty month period has been prepared for the Wainwright waterflood operation run by Husky Oil Operations Ltd. This database has been inspected by comparing averaged values for the measurements taken (APPENDIX A). Use of averages was necessary since not all measurements were taken at exactly the same point and time in each facility. Further, averaging tended to smooth out daily variations seen in the operations.

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3.1 Produced Water

The Wainwright field has been under production for decades and is currently produced by injection and recycle of water. The field is divided into a number of more or less self contained operating areas called units, each containing many production and injection wells. Each unit is equipped with facilities to separate produced oil and water (free water knock out, FWKO Figure 2) and reinject the water (waterplant, Figure 2). In the following sections, all downstream sampling points have been combined in "waterplant" averages while upstream data have been combined as "free water knock out".

Units of interest in this report are; 1, 5, 6, 12, 13 (location of field test facility), 14 and batteries 20 and 28. In addition a truckpit operation collects trucked oil from various sources in the surrounding area. The quality of fluids received here is variable and can be suspect. Produced water in the field is reinjected to support further production. Most units have source wells which can be used to augment injection water but most are of limited capacity. Only unit 14 shows a marked dilution of produced brine with fresh source well water, conductivity falls from 76 to 31 mS/cm in going from the free water knock out to the waterplant. Other units show less than 5% drop in conductivity.

Produced water handled in these facilities is a strong sodium chloride brine (conductivity, 47 to 76 mS/cm) of near neutral pH (6.5 to 7.0) rich in suspended solids (57 to 1600 mg/l) as well as oil and grease (182 to 10000 mg/l). Immiscible materials are highest at the free water knock out and drop markedly downstream of this unit. Sulfate concentrations are inversely related to soluble barium (Figure 3) due to the precipitation of barite. Battery 20 is an exception since a few anomalously high readings result in very high average sulfate values (APPENDIX A).

One curious feature is the relatively low sulfate levels seen at the free water knock cut (one tenth levels seen at the waterplant). Although temperature differences exist between these units (Figure 2), the independence of the free water knock out and waterplant barium/sulfate correlations is surprising (Figures 3B and 3C).

In general, the produced water chemistry is straightforward. Total hardness correlates directly with density, calcium concentration and conductivity and is inversely proportional to pH. These are expected correlations but again battery 20 gives anomalous results for unknown reasons.

3.2 Corrosion Monitoring

Over a thousand failures in the forty-two month period ending January 1991 cost in several million dollars in repairs and lost production. Failures specifically attributed to internal corrosion in the water handling system account for a significant fraction of this toll. Figure 4 shows that most corrosion failures occurred in battery 20 prior to day 400 on the plot. This reflects the banning of truckpit water from the unit at about this time. Apparently this water induced corrosive conditions in battery 20 operations prior to its banishment presumably due to its being "sour" (containing high soluble sulfide levels).

Seven parameters are used to track corrosion; soluble iron, soluble manganese, weight loss coupons, potentiodyne measurements (general corrosion rate and pitting index) and failures (frequency and cost). Attempts to correlate pairs of these parameters over some 30 months operation revealed little consistency

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between them.

The aim of any corrosion control program is to abate failures; yet, the only correlation seen between failure data and corrosion monitoring parameters was a correlation of potentiodyne pitting indices with failure frequency at the free water knock outs (Figure 5). Weight loss coupons, soluble metal ions and potentiodyne general corrosion rate measurements all failed to correlate with failure frequency.

The best correlation being found for the free water knock out data may be due to the fact that the water here comes directly from the oil reservoir and is yet to be greatly affected by oxygen exposure, chemical additions, mixing with other waters and microbial processes which can increasingly occur in the water handling facilities downstream of this point.

Weight loss coupons are a standard method of measuring corrosion rates through cumulative metal loss over time. Potentiodynamic measurements provide an instantaneous corrosion rate reading. In this case, rates are derived from Tafel plots showing the relationship of current and potential for a range of cathodic and anodic potentials applied to special probe tips mounted in the test system.

In this audit, a relationship was found between averaged general corrosion rates measured by these two techniques, Figure 6. Unfortunately, potentiodynamic measurements were several fold higher than weight loss measurements. This correlation all but disappeared when individual data points were considered in place of averages over many readings. The relationship seen was stronger for the waterplant data than for free water knock out data.

A second measurement derived from Tafel plots is a pitting index. A good correlation between the pitting indices and general corrosion rates obtained by potentiodyne may be rather trivial since both measurements are deduced from the same plot.

Soluble iron and manganese data were available from more than one source (APPENDIX A). Table 1 summarizes averaged soluble iron and manganese data corrected for anomalous measurements. As steel corrodes, these ions are released into solution. Using averages taken as part of the corrosion parameter monitoring program (APPENDIX A), the correlation in Figure 7 indicates that overall manganese is present at about 3% of the iron concentration consistent with source of both ions being corrosion of steel.

In all operations, the concentration of soluble iron and to a lesser extent manganese dropped in going from the free water knock out to the waterplant even when dilution by fresh makeup water at the waterplant is considered (Table 1). Loss of soluble iron and to a lesser extent manganese may be due to precipitation effects. Ferrous ion readily forms very insoluble sulfides or carbonate in anaerobic systems. Since the corresponding manganese compounds are less insoluble, iron can be selectively removed from solution. Elevated manganese to iron ratios suggest that preferential precipitation of iron is occurring in most units.

Correlations between soluble metal ions and other corrosion parameters were generally weak. Soluble manganese gave no correlation with corrosion rates measured by weight loss coupons. Modest positive correlation with potentiodyne measurements was seen using free water knock out or averages of all available data. Waterplant data specifically showed a negative correlation between corrosion rate and soluble manganese possibly due to precipitation effects such as the formation of manganese sulfides.

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Soluble iron behaved similarly.

In summary, there are few reliable correlations between parameters used to track corrosion. This means that field personnel must use combinations of parameters as relative indicators of corrosion in field systems. A significant degree of judgment is required since no single easily measured parameter can be used to optimize corrosion control programs. Long term plots of failure frequency and costs remain the final proof of efficacy.

3.3 Corrosion and Water Chemistry

Corrosion is an electrochemical process which depends on the presence of a good electrolyte. Figure 8 shows a correlation between failure costs and the conductivity of the produced water in the free water knock outs. A similar and more general correlation exists between water hardness and failure costs or failure frequency (Figure 9). In this case, hardness may reflect both the overall salinity of the brine and its capacity for scaling which can lead to differential corrosion cells and under deposit corrosion.

Suspended solids can also add to the capacity for surface deposits as well as carry noxious microorganisms and interfere with efficient chemical treatment in piping systems. A correlation between suspended solids and potentiodyne readings (pitting index and corrosion rate) was noted for all data and for the free water knock out specifically (Figure 10). Free water knock out data also supported a correlation with weight loss coupon corrosion rates (Figure 11). The loss of suspended solids in going from the free water knock outs to the waterplants precluded observation of these correlations in the downstream parts of the system. Oil and grease present in the water especially at the free water knock out correlate with failure costs (Figure 12). Again oil and grease may promote deposit formation and interfere with chemical corrosion control treatments. Hydrocarbons may also act as a food source for noxious bacteria in these systems.

Finally sulfate levels even where controlled by precipitation with excess barium seem to correlate with failure frequency in these systems, Figure 13. Although not shown on the plot due to the uncertainties in sulfate measurements and its peculiar failure history, the presence of periodic episodes of high sulfate at unit 20 and high failure rates both are seen in this unit. The impressive decline in corrosion failures after preclusion of truck pit water addition to unit 20 may have correlated with the occasional receipt of high sulfate waters free of barium rather than sour water (high in hydrogen sulfide) as previously supposed. These factors can be confused since one mechanism for the sulfate correlation could be production of hydrogen sulfide by the sulfate reducing bacteria prevalent in these systems.

3.4 Corrosion and Added Chemicals

Ammonium bisulfite is added to units in the Wainwright waterflood downstream of the free water knock outs to control oxygen corrosion. Residual sulfite is monitored to ensure complete treatment. Correlations obtained give a mixed picture of its performance.

Figure 14 shows an inverse correlation between residual sulfite levels and failure costs in the waterplant data suggesting that addition of oxygen scavenger is controlling corrosion. Unfortunately, both weight loss coupon and potentiodyne data (corrosion rates and pitting potentials) suggest the opposite (Figures 15 and

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16).

Corrosion inhibitor residuals correlate negatively with failure costs throughout these systems, Figure 17. In this case, there is no contradictory correlation between inhibitor residuals and corrosion rate data.

While both inhibitor and ammonium bisulfite addition appear warranted by failure cost data, residual sulfite levels also correlate with increased corrosion rates. This creates some doubt that ammonium bisulfite addition is the cause of reduced corrosion costs.

3.5 Microbiological Data

Surface bound biofilm populations of sessile bacteria are associated with increased corrosion risk (Pope, Duquetter, Wayner and Johannes, 1989; Jack, Worthingham and Ferris, 1991). Previous work at the field test facility, unit 13 waterplant has established that these systems are heavily fouled with microbial populations rich in sulfate reducing bacteria (Ferris, 1991). In the field wide audit, biofilm populations were characterized by determining the number of viable lactate utilizing sulfate reducing bacteria and acid producing bacteria present per cm^2 of pipe surface area. Unit 13 waterplant, the ratio of acid producing to sulfate reducing bacteria in the biofilm population has been a relatively stable characteristic for this unit and appears to represent some sort of optimum composition for the mixed bacterial population for the biofilm in this waterplant (Ferris, 1991).

The assay used for acid producing bacteria was developed in research programs sponsored by the Gas Research Institute, Chicago (Pope et al., 1989; Pope, 1991). Use of this assay has been proposed for identification and assessment of microbially induced corrosion scenarios in the oil and gas industry. The assay is based on a sugar fermentation. This will not encompass sulfate reducing bacteria since these organisms are unable to utilize complex nutrients like sugars. The assay does measure a wide range of other organisms and can be used as a general population index. Detection of an organism in this assay does not mean that organism was producing acid in the biofilm where sugars may or may not be available. The density of surface colonization varies over several orders of magnitude, APPENDIX A. In this situation, medians have been used in place of averages to represent population distributions.

In general, sulfate reducing bacteria are less numerous in the free water knock outs than in the downstream operations. Figure 18 shows distributions for the system at unit 1. Acid producing bacteria do not show such systematic variation.

Correlation of acid producing bacteria with sulfate reducing bacteria occurs for waterplant data (Figure 19) but not for free water knock outs. An interesting correlation occurs between the number of acid producing bacteria in a system and the increase in the density of sulfate reducing bacteria observed in going from the free water knock out to the waterplant, Figure 20. Since organisms counted as acid producing bacteria are able to handle more complex nutrients it is tempting to speculate that hydrocarbons are being broken down by these organisms to release simple fatty acids such as acetate or lactate which promote growth of the sulfate reducers. The quality of this correlation is sufficient that it is sustained even for individual pairs of measurements taken over time at a single unit (Figure 21). This is the first observation of a direct correlation between these types of organisms in a field system.

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3.6 Microbiology and Water Chemistry

Observation of changes in microbial numbers with variations in water chemistry at unit 13 waterplant revealed several correlations in the past (Ferris, 1991). Sulfate reducing bacterial counts were seen to increase with increasing sulfate but decrease with increasing nitrate and magnesium.

The field audit did not include nitrate measurements.

Inspection of field wide audit data here confirmed that lower numbers of viable sulfate reducers were found with higher magnesium concentrations at waterplants (Figure 22) but lower bacterial numbers were more generally associated with increasing hardness. This inverse correlation was found for acid producing bacteria at the free water knock outs and waterplants (Figure 23) as well as the sulfate reducing bacteria at waterplants (Figure 24). It may be that total brine strength is the limiting factor in these systems since hardness itself correlates very strongly with density and conductivity. In this situation, the prior observation that magnesium limited sulfate reducing bacteria at unit 13 waterplant may have reflected this overall salinity effect. There is no obvious reason why magnesium itself should be inhibitory at these concentrations.

High bacterial populations at the waterplant (both acid producing bacteria and sulfate reducing bacteria) coincide with higher pH (Figures 25 and 26). Alkaline conditions favour sulfate reducing bacteria and conversely these organisms tend to render growth media basic. The observation that the acid producing bacteria are also more numerous at higher pH however suggests that the organisms identified by this assay (fermentation of a sugar to acids) are not actively acidifying these field systems by their presence.

A correlation (Figure 27) between acid producing bacteria and suspended solids at the free water knock out suggests that these organisms are either being carried into the system on suspended particles (including oil in this measurement) or that such particles encourage growth of the sessile acid producing bacteria in the biofilm perhaps by providing nutrients. Suspended solids are rapidly lost in these systems so that waterplant levels are much lower than those seen at the free water knock outs, APPENDIX A.

A generally inverse correlation between residual oxygen and acid producing bacterial populations at the free water knock outs and at the waterplants (Figures 28 and 29) is consistent with the use of adventitious oxygen by these organisms. The higher the population, the lower the residual oxygen.

The previous observation that sulfate correlates with sulfate reducing bacterial numbers at unit 13 waterplant (Ferris, 1991) is reinforced in the field audit only for very low levels of sulfate (less than 2 mg/l). Figure 30 indicates that at higher sulfate levels found in waterplants, other factors must be limiting these organisms. This observation is notable since a generally accepted rule of thumb in corrosion control folklore is that sulfate reducing bacteria will not be a problem at sulfate levels below 100 mg/l. Clearly this is not the case here.

3.7 Microbial Numbers and Added Chemicals

Biocides were injected into these field operations over the course of the audit. No discussion of their effects will be included here. The observation that other parameters act on the biofilm populations with

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comparable potency was shown in Figure 1.

Residual sulfite from addition of ammonium bisulfite as an oxygen scavenger and residuals of phosphate rich scaling inhibitors both correlated with increased populations of acid producing and sulfate reducing bacteria at the waterplants (Figures 31 to 34). No such correlation was found for free water knock out populations possibly since these chemicals are usually injected downstream of these units, Figure 2.

Free water knock out sulfate reducing bacterial populations did correlate with corrosion inhibitor residuals (Figure 35). It is tempting to suggest that nitrogen, phosphorus and sulfite/sulfate are being provided to the microbial biofilm communities by addition of these control chemicals; however, correlations can be deceptive. It may be that the systems which give most trouble and are richest in organisms receive higher dosages of control chemicals.

3.8 Microbial Numbers and Corrosion

Figure 36 shows a general correlation between corrosion rates observed by weight loss coupons and the increase in sulfate reducing bacterial populations in these systems. A correlation also exists between the number of sulfate reducing bacteria in the biofilm of the free water knock outs and weight loss data. This supports the use of sulfate reducing bacterial numbers as the index of biocide performance in these systems.

No other positive correlation between microbial numbers and corrosion rates or failure data was found. It should be noted that these systems are under treatment by corrosion control additives including biocides. This may of course mask relationships which might be otherwise evident.

3.9 Summary of Audit Findings

Water handling facilities in the Wainwright waterflood separate and reinject high salinity brines in which excess barium controls sulfate solubility. Sulfate levels are remarkably low in the free water knock outs but increase modestly downstream in the waterplants.

Unit 14 is unusual in that fresh makeup water cuts the salinity of the brine in the downstream units. This does not seem to influence the fit of this unit on the numerous correlations done in this study.

Unit 20 does tend to be exceptional. While this can be explained in terms of the removal of truckpit water in terms of its corrosion record in the past, deviation from correlations seen for other units since that time are not so easily rationalized.

Truckpit waters are received from a wide range of sources. It is expected therefore that this operation will tend not to be well behaved with respect to units handling only Wainwright water.

There is no corrosion monitoring technique which can be used to optimize corrosion control programs. The only correlation observed between corrosion monitoring parameters was between the potentiodyne pitting index at the free water knock out and overall failures.

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Potentiodyne measurements only approximately correlate with weight loss coupon results. Soluble iron and manganese correlate overall with manganese at about 3% of iron levels. This correlation weakens downstream in the units as precipitation effects become apparent.

Conductivity and hardness at the free water knock out correlate with failure data presumably due to the tendency of salinity and deposits to promote corrosion. Suspended solids and oil and grease also correlate with failure data again suggesting deposits are detrimental and inferring that hydrocarbons may be promoting undesirable bacterial fouling effects. Sulfate despite its low concentration also correlates with failures, again suggesting that action by the sulfate reducing bacteria is related to corrosion damage. The increase in sulfate reducing bacteria from free water knock out to waterplant is related to overall corrosion rate measurements by weight loss coupon.

The addition of excess oxygen scavenger and corrosion inhibitor correlate with reduced failure data; however, the correlation of residual sulfite with increased corrosion rates weakens confidence that the oxygen scavenger is causing the reductions seen. Both sulfite and scaling inhibitor residuals plot with increased bacterial populations at the waterplants. Corrosion inhibitor residuals correlate with the sulfate reducing bacterial population but only at the free water knock outs. It is possible that these chemicals are fostering bacterial growth by providing the nitrogen, phosphorus and sulfite/sulfate needed for metabolism.

Overall salinity seems to be limiting bacterial populations growing on the piping surface in the waterplants. Hardness and magnesium concentration are specific indicators for this limitation. Higher bacterial numbers correlate strongly with pH even though the range observed is less than 0.5 pH units.

The mixed bacterial populations present in the biofilm have been characterized by a general assay for organisms able to ferment sugar to acids (acid producing bacteria) and by a specific assay for anaerobic sulfate reducing bacteria. The ratio of these has proven to be stable in past work at unit 13 waterplant indicating that optimal compositions exist for these mixed populations in a given environment. A correlation does exist over the whole field between acid producing bacterial numbers and sulfate reducers in the waterplants. An even stronger relationship however is seen between the acid producing bacteria present and the increase in sulfate reducing bacterial numbers through these water handling facilities. This correlation is sufficiently robust that it is strongly evident even for individual data pairs taken over time at a single unit. In the free water knock out where sulfate levels are less than 1 mg/l, sulfate availability correlates with sulfate reducing bacterial densities. In waterplants however other factors seem to be limiting growth.

In the free water knock out suspended solids (a measurement including hydrocarbons) correlates with the number of acid producing bacteria present. It is possible that these organisms are using the hydrocarbon as a nutrient. This is consistent with an inverse correlation seen between residual oxygen and acid producers which would require oxygen for the rapid metabolism of oil. In this scenario, a break down of oil by acid producing bacteria would provide small organic acids used by sulfate reducing bacteria. This is consistent with the observation that the extent of increase in the sulfate reducing bacterial population in going from the free water knock out to the waterplant is a function of the acid producing bacterial numbers present. In this case, the limiting factor on growth of the sulfate reducing bacteria at the waterplant should be organic acids like acetate or lactate.

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In the next section of this report, an experimental program is described for the NHRC field test facility at unit 13 waterplant. In the study reported here, the dependence of bacterial populations and corrosion rates on the concentration of nitrate, acetate/lactate and oxygen scavenger was investigated.

4.0 FIELD TEST FACILITY - METHODS

The NOVA HUSKY Research Corporation (NHRC) field test facility in its new mobile trailer was reinstalled at Unit #13 waterplant in the Husky Oil, Wainwright water injection system near Wainwright, Alberta. This field test facility is unique in Canada, and permits monitoring of natural microbial biofilms on five separate flow lines. Water from the field injection system enters the test facility where an independent pumping and metering system allows flow rates to be selected independently for each line. Effluent water is returned to the field injection system and is not recycled. There are 40 removable coupons and individual injector systems on each line to permit *in situ* monitoring of biofilm responses to various chemicals (e.g. biocides) at selected dosages. The field test facility is instrumented to determine the extent of biofouling from the pressure drop across test lines and is equipped with potentiodyne probes and weight loss coupons to measure corrosion rates.

For this investigation, the NHRC field test facility was equipped with 0.95 mm diameter carbon steel coupons for routine sampling of surface deposits including biofilm inside the water piping.

During the first 63 days of the experimental run, from October 8 to December 10, 1991, untreated water from the injection system was allowed to run through the five separate test lines. This period was used to establish a biofilm (surface) bacteria within the system prior to chemical injections. This long colonization period was required since the entire unit had just been rebuilt as part of its conversion into a mobile trailer facility. Previous work suggests that such lengthy periods are needed to establish mature biofilms in clean piping in this field (Jack *et al.*, 1991, in press).

4.1 Chemicals

Chemical treatment commenced on December 10, 1991 and continued to approximately February 18, 1992, a period of about 70 days. Chemicals added included sodium nitrate (CDL Limited, Calgary), sodium sulfate (McKenzie and Feinmann, Edmonton), sodium acetate (McKenzie and Feinmann, Edmonton), sodium lactate (60% syrup, Aldrich, Milwaukee, Wisconsin) and ammonium bisulfite oxygen scavenger (Wellchem CO8614, Wellchem Ltd, Lloydminster, Alberta). Table 2 shows chemical injections for each line. Both planned and actual treatments are tabulated. This will be discussed in the "Results" section in greater detail.

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4.2 Sample Collection and Processing

4.2.1 Sampling For Microbiological Testing and Scanning Electron Microscopy

Just prior to chemical injection, specific carbon steel coupons from the field test facility were removed from all five lines according to a schedule set up for field personnel. After removal, the coupons were placed into labeled, sterile plastic vials which were subsequently filled with untreated injection water from the injection system. These vials were then shipped to Calgary by air-freight for processing at NHRC. At NHRC, the coupons were placed in a Forma Scientific Model 1024 anaerobic chamber to protect the samples against further oxygen exposure.

For microbiological assays, exposed surfaces of the sample coupons were scraped using sterile scalpel blades to remove attached microorganisms. The residue recovered from the coupons was then placed into tubes containing 10 ml sterile Postgate minimal salts medium supplemented with 1.0 % (w/v) NaCl (Postgate, 1984). The tubes were subsequently sonicated for 5 minutes using a Bransonic 32 sonicator to disrupt aggregates of bacterial cells.

4.2.2 Sampling for Water Analyses

At the same time the coupons were sampled, water samples were collected from each line in large 1 litre plastic bottles. An extra sample from line 1 and 2 was collected in 250 ml glass bottles. The water samples were shipped to Calgary with the coupons for analysis.

Sampling for sulfite residuals was also performed on water taken from line 5 by Mr. Clare Clemmer, Wellchem Ltd. Water samples were taken at scheduled intervals during chemical injection from two locations: one was at the header located on the field test facility just upstream of the five flow lines; the other was directly off line 5 below the chemical injection point. These sampling points gave background and treatment levels of residual sulfite, in line 5.

4.3 Microbiological Analyses

4.3.1 Lactate Utilizing Sulfate Reducing Bacteria

The method used to enumerate sulfate reducing bacteria (SRB) was the Most Probable Number technique (MPN). Serial dilutions from 10^{-1} to 10^{-8} were prepared by adding 0.5 ml of the sample suspension to tubes containing 4.5 ml of Postgate B medium, 1% NaCl (w/v) (Postgate, 1984). The tubes were then incubated at 25° C for up to 21 days. Blackening of a tube due to iron sulfide formation was a positive test for the growth of sulfate reducing bacteria. Standard probability tables were then used to express the number of positive tubes as viable SRB per cm^2 of sample coupon surface.

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4.3.2 *Acetate Utilizing Sulfate Reducing Bacteria*

A very complex medium (Collins and Widdel, 1986) was prepared for growth of acetate utilizing bacteria (APPENDIX B). The technique for enumerating acetate utilizing SRB was the same as for lactate utilizing SRB. That is to say, a serial dilution from 10^{-1} to 10^{-8} was conducted in triplicate for each sample. Tubes were incubated also for twenty-one days. Samples from tubes were examined microscopically to determine the extent of growth because it was found that viable cells were observed without the tubes turning cloudy. The same calculations were performed on these samples as were done for the lactate utilizing SRB.

4.3.3 *Radiolabelled Sulfate Reduction Activity Assay*

The activity of the SRB was assessed by adding 1.0 ml aliquots of sample suspensions to tubes containing 1.0 ml Postgate C medium, 1% NaCl (w/v) and 0.8 uCi/ml of ^{35}S-sulfate (Postgate, 1984). A cup containing a paper wick saturated with 0.5 ml of 1.5 M zinc acetate was suspended from rubber stoppers in each tube to trap evolved H_2S. The assays were terminated after six hours incubation at 25° C by adding 1.0 ml of 6 M HCl to each tube. After an additional 24 hours, the wick-cup assemblies were removed and placed into 10 ml of scintillation fluid. These samples were then counted a day later using a Rack Beta Model 1211 scintillation counter, and the µmoles H_2S produced/cm^2 day calculated.

4.3.4 *Enumeration of Acid Producing Bacteria*

Acid producing bacteria (APB) were enumerated by serial dilution of sample suspensions and water from 10^{-1} to 10^{-7} into proprietary APB medium, 3% NaCl (w/v) (Bioindustrial Technologies Inc., Grafton, New York, U.S.A.). The growth of APB was revealed by a change in culture medium color from red to yellow; the number of APB in the original samples was then calculated from the highest dilution at which growth occurred. This assay is based on the production of acid from glucose under anaerobic conditions turning the colour of a pH indicator (Dr. David Dziewulski, BTI, personal communication).

4.3.5 *Scanning Electron Microscopy*

Scanning electron microscopy (SEM) was performed on the exposed surface of coupons removed from the field test facility. To prepare the surface of each coupon for SEM, a series of extractions with ethanol and freon were necessary. Concentrations of 20%, 30%, 50%, 70%, 90%, 95% and 100% ethanol were made up with distilled water. Each coupon was immersed in each concentration for five minutes, starting with the lowest, and working towards the most concentrated dilution of ethanol. Immediately following this, another series of extractions were performed in freon, diluted with ethanol. The concentration series used was the same as for ethanol and water, except there were three immersions into 100% freon in the end in place of only one immersion into 100% ethanol. The coupons were removed from the third 100% exposure to freon and allowed to air dry.

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Immediately prior to examination by SEM, the surface of each coupon was coated with a layer of gold using an Edwards Sputter Coater S150B. Examination of the gold-sputtered surfaces was performed with an Hitachi S-2500 SEM operating at 15 kV. The SEM was equipped with a Tracor Northern energy dispersive X-ray spectrometer. Energy-dispersive X-ray spectroscopy (EDX) was conducted in the selected area electron beam raster mode, and spectra were obtained by collecting counts for up to 200 seconds (live time).

4.3.6 DNA Probes

Identification of certain acetate, lactate and benzoate utilizing sulfate reducing bacteria previously isolated from the Wainwright oilfield (Voordouw *et al.*, 1991) was carried out by Professor G. Voordouw and his staff at the University of Calgary.

4.4 Water Chemistry

Water samples from all five lines were assayed for the following cations: sodium, potassium, calcium, magnesium, and iron. The following anions were also assayed for: chloride, sulfate, sulfide, nitrate and bicarbonate. Cations and anions were analyzed in six samples taken from each line throughout the experimental run at the field test facility, except for Line 1, where nitrate was not assayed in the first sampling. Lines 1 and 2 were analyzed intermittently for total Kjeldahl nitrogen. These analyses were done by Chemical and Geological Laboratories Inc., Calgary.

4.4.1 Acetate and Lactate in Line 4

Additional analysis for lactate and acetate was performed on water samples from Line 4. Five samples were taken over the course of the experimental run. The analysis for these two fatty acids was performed at Chemex Laboratories, Calgary. Confirming analyses for acetate were carried out at NHRC on acidified samples using a Varian 6000 gas chromatograph equipped with an FID detector using an FFAP CP capillary column with injection and column temperatures of 250°C and 125°C respectively. Helium gas at a flow rate of 44 cm/sec was the carrier gas. A split ratio of 35:1 was used.

4.4.2 Residual Sulfite in Line 5

Residual sulfite analyses were performed on water samples from line 5 for residual sulfite by Mr. Clare Clemmer of Wellchem Inc., Lloydminster, Alberta using a Hach kit.

4.5 Corrosion Rate Measurements

4.5.1 Potentiodynamic Measurements

Potentiodynamic polarization measurements were performed four times at the field test facility using a

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Petrolite model M 4100 potentiodyne analyzer. General corrosion rates were determined from current density values at the intersection of cathodic Tafel slopes and open circuit potentials. Pitting tendency rates were estimated from current density values at the intersection of cathodic Tafel slopes and return anodic curves.

4.5.2 Corrosion Weight Loss Measurements

Two types of coupons were used for weight loss determinations. One type was the standard rod-type weight loss coupon, made of 1018 carbon steel. These coupons were purchased, pre-weighed and pre-cleaned from United Corrosion Ltd., Edmonton. These coupons were mounted into elbow fittings located downstream of the coupon-sampling units on each line. Two sets of weight loss coupons were used. One set was installed for the baseline colonization of the test facility and removed immediately prior to chemical addition. A second set was installed for the experimental run.

The three electrodes on the potentiodyne probe in each line were also used as weight loss coupons. These electrodes were purchased from United Corrosion Ltd., Edmonton. These electrodes were made of 1018 carbon steel, and were pre-weighed prior to installation. Potentiodyne electrodes were used to obtain three weight loss measurements over the experimental period; one immediately prior to chemical treatment and two during chemical treatment.

4.5.2.1 Cleaning and Weighing

Both types of coupons were cleaned using a coarse brush and an inhibited acid cleaning solution called Clarke's solution composed of: 20 g antimony trioxide plus 50 g stannous chloride in 1000 ml concentrated HCl. 250 ml aliquots were poured into 500 ml beakers for the cleaning process. The cleaning process began with scrubbing off deposit that was not solidly attached to the coupon/electrode surfaces with the fibrous brush. Each coupon/electrode was then dipped into a beaker of dichloromethane to remove any oil from the surface. The coupon/electrode was then immersed in Clarke's solution for 30 seconds for removal of attached deposits. The coupon/electrode was quickly removed and immersed in a beaker of distilled water. Following this, the coupon/electrode was washed twice in acetone and air dried then weighed using a Mettler AE 100 balance. This procedure was repeated to more or less constant weight.

5.0 FIELD TEST FACILITY RESULTS

5.1 Field Test Facility Program

The field test facility is equipped with five instrumented slip streams which take in water from the injection stream of an operating oilfield waterflood. Flow through the five lines can be independently regulated with respect to flow rates and independently dosed with nutrients and chemicals as shown in Table 2.

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Line 1 had nitrate added. A previous study in the field test facility had suggested that the sulfate reducing bacterial population had varied with fluctuations in nitrate concentration observed in the water flow (Ferris, 1991, Jack *et al.*, in press).

Line 4 had acetate and lactate added to it to test the hypothesis that sulfate reducing bacteria are limited in the waterplant by the availability of suitable organic nutrients.

Line 5 had ammonium bisulfite oxygen scavenger added to test the hypothesis that sulfate limitation on the sulfate reducing bacterial population might be alleviated by its use. A modest dependence of sulfate reducing bacterial numbers on soluble sulfate had been noted previously in the field test facility (Ferris, 1991, Jack *et al.*, in press). Correlation of residual sulfite with sulfate reducing bacterial populations in the field audit described above supported this hypothesis.

The original intention to add sodium sulfate to line 2 was thwarted by copious precipitation with the excess barium found in these waters. Fear of plugging the injection pump or worse the formation face at the injection well resulted in this intention being abandoned in favour of looking at the effect of a transition to laminar flow on the microbial fouling. The line was set at a laminar flow rate as shown in Table 2 commencing December 25, 1991 (Day 15).

5.1.1 Water Chemistry

Complete water analyses over the course of the study can be found for each line in Appendix C. The water flowing through the facility is about a 5.8% brine.

Analysis of injected chemical concentrations in water samples may have suffered from sampling problems related to skid shutdown for coupon removal. Injection of a concentrated stock solution into the water flow in each line is accomplished by a controlled rate injection pump. Water samples were taken at the same time as coupon removal which necessitates shut down of the water flow. If water samples are taken with water flow turned off then accurate solution concentrations will not be found for injected chemicals since it is very hard to shut down both the main pump and all the chemical injector pumps simultaneously. An early shut down of the injection pumps allows fresh water to flush the line while a late shut down means that excess concentrated stock solution is being pumped into the stagnant line. Better protocols are needed for water sampling for injected chemical analysis in the field test facility. Based on the amount of chemical actually used, concentrations have been calculated assuming even injection over the test period (Table 2). These numbers are probably more accurate than measurements of injected chemical concentrations.

Nitrate levels were highest in line 1 due to injection of sodium nitrate. Table 2 gives calculated injection levels. Depletion of stock solution before the final sampling after February 18th (Day 70) is evident in Figure 37.

Acetate and lactate levels (Table 3) were a few parts per million in the control but showed considerable

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elevation due to injection in line 4. The inconsistent pattern evident in acetate concentrations may indicate sampling problems as noted above. Table 2 shows calculated values.

Injected oxygen scavenger (ammonium bisulfite) levels are given in Table 2. Sulfite levels (Figure 38) show that the appetite of line 5 for the added sulfite may have increased over the test period lessening the excess of outlet over inlet concentration.

Twenty fold fluctuations in sulfate were noted as in a previous study (Ferris, 1991). Initially elevated levels were seen in line 5 to which a bisulfite oxygen scavenger was being added but this fell to lower than usual levels after January 18th (Day 39) (Figure 39). Oxidation of oxygen scavenger as it reduced the environment in line 5 may have resulted in the excess sulfate seen early in the test period. In general, soluble sulfate levels are controlled by excess barium in these brines which precipitates barite.

Sulfide levels were lowest in line 1 consistent with an inhibition of microbial sulfate reduction in the presence of nitrate, Figure 40.

5.1.2 Corrosion Data

Corrosion rates from potentiodyne scans are presented in Table 4. At the end of the colonization period, 92/12/09, potentiodyne probe tips were replaced with new electrodes. A repeated scan with the new electrodes in control line 3 indicated little influence of biofilm on the reading. The colonized probes gave a general corrosion rate of 0.014 mm/year compared to 0.017 mm/year. By 92/01/30 (Day 51 of the test run), line 1 (+nitrate) probe tips were described as severely fouled (6 mm) compared to the other cases which developed only moderate sludge buildup (2 mm). Line 1 nitrate addition gave corrosion rates an order of magnitude higher than other cases.

Corrosion rates were also measured by weight loss coupons and by using the potentiodyne probe tips as weight loss coupons. The latter gave inconsistent and variable results possibly due to the effect of scans on the electrodes and were therefore ignored. The weight loss coupons gave relative corrosion rates showing line 1 an order of magnitude higher than other lines as was seen also for the potentiodyne measurements, Table 4. While the pattern of corrosion rates over the five test lines was the same for potentiodyne and weight loss coupons the absolute corrosion rates did not agree. Potentiodyne scans gave rates much higher than seen for the coupons. This is consistent with results in a previous project (Ferris and Bramhill, 1990) in which corrosion rates by potentiodyne could only be used as a relative index of corrosion. Actual readings obtained by potentiodyne were unrealistically high (up to 33 mm/year).

No significant difference in corrosion rate was evident for either laminar flow (line 2) or acetate/lactate (line 4) or oxygen scavenger addition (line 5) compared to the turbulent flow control case (line 3). Potentiodyne corrosion rate measurements constantly increased over the test period for these cases despite replacement of the probe tips at each reading date (Table 4).

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5.1.3 Microbiology

Inspection of microbial numbers in the audit data described above showed that these populations exist as distributions over several orders of magnitude. This makes accurate measurement by one or two sample analyses unlikely. All samplings were therefore done in quintuplicate for this report. Figures 41 to 47 show median values for the five replicates while Figures 48 to 50 use means. There are differences. Where populations are spread over several logs, the average or mean value is unduly weighted by the largest number in the distribution even if it is anomalous relative to the other replicates. Median values are thus better representations of biofilm populations than means.

Figures 41 to 45 show the viable cell counts for lactate and acetate utilizing sulfate reducing bacteria as well as acid producing bacteria by line.

In line 1 (Figure 41) nitrate has suppressed the lactate utilizing sulfate reducers as well as the acid producing bacteria. Acetate utilizing sulfate reducers do not seem so affected. This is partly corroborated by DNA probe analysis, Table 5. Here detection of four isolates obtained from Wainwright facilities showed that the acetate utilizer Ace1 may have been slightly enhanced by nitrate addition over the control but only one of two lactate utilizing sulfate reducers appeared to be similarly affected.

A switch to laminar flow seems to have little effect on microbial numbers (Figure 42 compared to Figure 43).

Addition of acetate and lactate to line 4 resulted in the highest populations of sulfate reducing bacteria seen (Figure 44). This suggests that both sorts of SRB are under organic nutrient limitation and respond to even minor increases in nutrient concentrations. The late response of the acetate utilizing sulfate reducing bacteria may correlate with the uneven addition of this nutrient. Considerable handling difficulty was experienced with the sodium acetate which came as a fine powder, difficult to pour and dusty to handle. Some effort was required to work out a tolerable procedure for making up stock solutions in the field. This may have resulted in lower than desired injection levels early in the run. The increase in both acetate and lactate utilizing sulfate reducing bacteria is confirmed by DNA probe assays (Table 5).

Line 5 (Figure 45) showed a slight increase in lactate utilizing sulfate reducing bacteria over the control (line 3, Figure 43). This would be consistent with use of the residual sulfite or its oxidation product, sulfate by these organisms.

Figures 46 and 47 compare lactate and acetate utilizing bacterial numbers respectively for the various lines. For lactate utilizers (Figure 46) stimulation is seen for line 4 (+acetate/lactate) and line 5 (+oxygen scavenger). Inhibition is seen for line 1 (+nitrate). Laminar and turbulent flow controls are similar. For acetate utilizers (Figure 47), nitrate may have been inhibitory but only a modest difference was seen with respect to control line 3 and line 5 (+oxygen scavenger). Acetate/lactate addition (line 4) was again stimulatory. All these effects were achieved by addition of nutrients in the ppm range indicating the potent

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influence of even minor fluctuations in nutrient levels on biofilm populations at the waterplant.

Sulfate reduction rates measured in lactate medium for biofilm populations in the lab are given in Figures 48 to 50. A general correlation with the trend in viable numbers of lactate utilizing sulfate reducing bacteria is seen in lines 1 (nitrate addition) and 3 (control). The switch to laminar flow for control line 2 appears to diminish sulfate reducing ability but more data would be needed to confirm this conclusion.

5.1.4 Scanning Electron Microscopy

Figure 51 for line 2 control shows surface deposits typical of all coupons examined. At low magnification, areas of thin flat deposits cover much of the coupon face. Thicker deposits with a smooth appearance and "spongy" areas represent the major volume of deposits. This is consistent with the observations made previously (Ferris 1991; Ferris, Jack and Bramhill, submitted).

Biofilms formed in turbulent and laminar flow have been previously observed to be quite distinct in their physical characteristics (McCoy *et al.*, 1981). Failure to observe any change in the physical appearance of the biofilm after moving to laminar flow in line 2 suggests that biofilms formed in turbulent flow in the field are insensitive, at least to short term reductions in flow rate.

Detailed high magnification micrographs show significant differences in the composition of the biofilm in line 1. Microorganisms were abundant and apparent (Figure 52). Close inspection revealed that cell surfaces were encrusted with deposits, possibly dehydrated capsular material. Energy dispersive X-ray analysis showed the presence of iron and calcium in the deposits but no sulfide (Figure 53). This contrasted to other lines which showed sulfide (Figure 54, Line 3, control) along with iron indicating iron sulfide as a major corrosion product. This is typical of the iron sulfide/sulfate reducing bacterial corrosion mechanism previously described for these systems (Jack, Worthingham and Ferris, 1991).

Calcium was frequently present. In the absence of sulfide the anion for calcium and iron could be oxide, carbonate or anionic biopolymer (slime) associated with the biofilm. Given the predominantly anaerobic condition of the facility, carbonate or anionic biopolymer seems most likely. A few drops of dilute HCl placed on coupon deposits gave strong effervescence consistent with the presence of carbonates for all coupons. Line 2 gave a marginal response while line 1 (nitrate addition) bubbled strongly. Other cases gave intermediate response with line 4 (acetate/lactate addition) being somewhat more positive. This evidence of carbonate deposition is consistent with the use of scaling inhibitors elsewhere in this field and suggests that calcite deposition may be occurring along with formation of the less soluble iron (II) carbonate or siderite, as the favoured corrosion product under anaerobic conditions.

The control lines 2 and 3 and the oxygen scavenger line 5 all had surface deposits essentially the same as those reported in previous studies at the field test facility (Ferris, 1991).

Increased biopolymer (slime) production on addition of acetate and lactate in line 4 (Figure 55) gave a lacy

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appearance to parts of the dehydrated specimen. Energy dispersive X-ray analysis of areas of distinctive mineralization showed the presence of iron sulfide (Figure 56).

Analysis of surface deposits showed chloride in only one feature (line 5). This either reflects the ease of washing away excess chloride from the surface of the specimen during sample preparation or reflects an intrinsic feature of chloride distribution within the biofilm. Recent studies on corrosion nodules conducted for the Gas Research Institute, Chicago, indicate that chloride is not uniformly distributed but is concentrated in specific layers within corrosion deposits (Pope, 1991). Previous work on biofilms in the system at Wainwright (Ferris; 1991, Ferris, Jack and Bramhill, submitted) suggests that chloride is unevenly distributed to charge balance non-stoichiometric iron sulfides in various states of maturity.

6.0 CONCLUSIONS

6.1 Corrosion Monitoring

Correlations in audit data between corrosion monitoring parameters are almost non-existent. This means that field corrosion personnel must use a combination of indicators interpreted through their experience to optimize corrosion control programs. Long term plots of corrosion frequency and cost remain the only real proof of efficacy.

Potentiodyne measurement of corrosion rates only generally correlates with corrosion weight loss coupon data. Time averaged soluble iron and manganese levels do correlate in a global sense with manganese being about 3% of iron concentration but local measurements can be compromised by precipitation effects.

6.2 Corrosion and Water Chemistry

Failure frequency or cost correlates with high produced water salinity, hardness, suspended solids, oil and grease and soluble sulfate levels. This last correlation is interesting since soluble sulfate is limited by precipitation with excess barium to very low concentrations. The increase in the density of sulfate reducing bacteria in the biofilms in going from free water knock outs to waterplants correlates with corrosion rates measured by weight loss coupons.

The addition of corrosion inhibitor correlates with reduced failures, has no relationship with measured corrosion rates and corresponds to elevated counts of sulfate reducing bacteria in the free water knock out.

Residual sulfite from the addition of oxygen scavenger correlates with lower failure costs but increased corrosion rate data. Sulfite also correlates with increased bacterial biofilm densities in waterplants. Experimental results from the field test facility confirm increased densities of lactate utilizing sulfate reducing bacteria result from addition of oxygen scavenger but no change in corrosion rate resulted from its addition.

Use of scaling inhibitor corresponded to increased bacterial densities in waterplant biofilms.

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Corrosion and scaling control chemicals may be providing a source of nitrogen, phosphorus and sulfite/sulfate for the bacterial populations in these units. In providing nutrients, these additions may foster microbial growth in opposition to the intent of biocide additions intended to disinfect a system.

6.3 Factors Controlling Bacterial Populations

In addition to the possible promotional effect of added control chemicals, water salinity/hardness and pH were found to have important correlations with sessile bacterial population densities. Conductivity, hardness and soluble magnesium concentrations all correlate inversely with bacterial densities in the waterplant biofilms. Apparently these populations may be limited by the salinity of the produced brine. Bacterial numbers also strongly correlate with increased pH even over a narrow range of 0.5 pH units. The strength of this correlation is surprising given the narrow pH range involved. The inverse correlation of high numbers of acid producing bacteria with increased pH clearly indicates that these organisms are not affecting the pH of these systems. Since the assay which identifies this group of organisms is the fermentation of a sugar to produce organic acids, a very broad group of organisms is included in this designation. It is not clear that they are necessarily acidifying the biofilm in the field units.

The correlation of acid producing bacteria with suspended solids entering the free water knock out and their general inverse correlation with residual oxygen suggest that they may be utilizing oxygen to attack complex organic materials such as hydrocarbons. Release of organic acid moieties such as acetate or lactate by the general population would promote anaerobic sulfate reducing bacteria by providing the simple nutrients they require.

This view is supported by the correlation of acid producing bacterial numbers with the increase in sulfate reducing bacteria found between the free water knock outs and downstream waterplants. Addition of low levels of acetate and lactate to one leg of the field test facility confirmed that the sulfate reducing bacteria at unit 13 waterplant are limited by organic nutrients. Sulfate may limit the sulfate reducing bacterial population at the free water knock outs where sulfate levels are less than 1 mg/l. The common idea that water systems with less than 100 mg/l sulfate will not support extensive populations of sulfate reducing bacteria is clearly at variance with the data seen here.

A shift from turbulent to laminar flow in the field test facility had little effect on viable bacterial numbers although some loss of sulfate reducing ability on a lactate based assay medium may have been evident.

The addition of low concentrations of nitrate has been observed to inhibit sulfate reducing bacteria and its use has been suggested as a way to control their activity (Jack *et al.*, 1985; Jenneman *et al.*, 1986). Addition of 100 mg/l sodium nitrate to one leg of the field test facility suppressed the sulfate reducing bacterial populations at unit 13 waterplant confirming earlier observations (Ferris, 1991). No iron sulfide was detectable in surface deposits taken at the end of a 70 day run. Nevertheless, thick biofilms rich in bacteria were observed along with significantly increased corrosion rates which may have been related to the enhancement of a nitrate respiring microbial consortium. Nitrate reducing bacteria have been implicated in the internal corrosion of water piping (Caldwell and Ackerman, 1946; Tuovinen and Hsu, 1982). Proposed mechanisms of action include both cathodic depolarization (Mara and Williams, 1971; Umbreit, 1976) and organic acid production (Ashton, Miller and King, 1973). Rajagopal *et al.*, 1988, have reported that *Desulfovibrio* species can use nitrate in place of sulfate as the terminal electron acceptor if

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cathodic hydrogen is available and that maximum activity occurs when lactate is limiting. Thus common sulfate reducing bacteria may be among the organisms promoting corrosion in this study where added nitrate exceeds available sulfate. This suggests that adding nitrate to a system colonized by sulfate reducing bacteria under lactate and sulfate limitation can be dangerous. The nitrate itself is benign with respect to pitting of passivated iron surface (Ogura and Ohama, 1981) and when reduced to nitrite may even promote passivating oxides (Obuekwe, Westlake and Cook, 1981; Ashton, King and Miller, 1973). The high corrosion rate observed at unit 13 waterplant precludes use of nitrate as a control chemical for use in this field.

The sensitivity of the mixed populations at unit 13 waterplant to addition of organic or inorganic nutrients at the mg/l level indicates that the nutrient flux within this mixed community probably plays a key role in explaining its variability under biocide treatment. The relatively rapid shift to a more corrosive population on nitrate addition suggests that more or less corrosive populations do exist and that it may be possible to alter water chemistry and additives to achieve better fouling and corrosion control. Given the economic impossibility of sterilizing field systems through biocide addition, a better understanding of controlling populations and their impact by more subtle means may be the only way to increase performance in these field systems beyond the present state of the art.

7.0 RECOMMENDATIONS

- Reassess use of ammonium bisulfite as an oxygen scavenger.
- Continue use of corrosion inhibitor and where necessary scaling inhibitor.
- Control nitrate levels where possible.
- Assess new corrosion monitoring approaches in an effort to find a method which can accurately predict corrosion failure.
- Investigate the practicality of discouraging sulfate reducing bacteria through alteration of water chemistry or by reduction of the availability of nutrients. Possibilities include; reduction of pH (to 6.5) reduction of factors (oxygen, suspended solids) promoting bacteria which feed the sulfate reducers and reduction of incremental sulfate entering the waterplants.
- Seek to identify and propagate benign biofilm populations. This will require improved assay procedures for the characterization of microbial populations.
- Apply multi-variate statistics (instead of seeking simple binary correlations) in the audit database to understand the interaction between the parameters better.
- Inspect audit data on a unit by unit basis using the correlations obtained here along with biocide

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injection data to understand factors influencing corrosion and fouling control in the Wainwright field.

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9.0 TABLES

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Table 1: Summary Soluble Iron and Manganese Averaged Data									
	Iron (mg/l)		Manganese (mg/l)		Mn/Fe		Ratio (WP/FWKO)		
	FWKO	WP	FWKO	WP	FWKO	WP	Iron	Manganese	Conductivities (µS/cm)
Unit 1	11.9	10.2	0.28	0.21	2.2	2.3	.86	.75	.95
5	11.6	9.5	0.31	0.28	2.8	4.3	.82	.90	.98
6	10.1	7.7	0.37	0.31	4.2	4.0	.76	.84	1.0
13	9.3	--	0.56	--	5.4	--	--	--	--
14	26.8	8.0	0.42	0.25	1.5	3.3	.30	.60	0.41*
Battery 20	11.8	8.1	0.40	0.36	4.0	4.9	.69	.90	1.01
28	8.0	6.7	0.40	0.36	5.3	5.8	.84	.90	1.02
Truckpit	--	12.4	--	0.57	--	6.6	--	--	--

* Unit 14 shows substantial dilution of the brine by fresh water make up at the waterplant.

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Table 2: Experimental Program in the Field Test Facility

Line	Chemical	CONCENTRATION (ppm)		Flow Rate (m^3/day)	Reynold's Number Re
		Planned	Actual		
Line 1	sodium nitrate	100	100[1]	37.9	20,919
Line 2	sodium sulfate	120	Control no chemical added - laminar flow[2]	2.16	1,192
Line 3	Control turbulent flow	no chemical injected	Control	39.2	21,638
Line 4	sodium lactate sodium acetate	35 100	16[1] 45[1]	37.9	20,919
Line 5	sodium bisulfite	75 - 100	75 - 100[1]	40.3	22,244

1. Calculated concentration based on total chemical actually used/total measured volume of water flow over the test period.

2. Problems encountered with sodium sulfate addition caused a change of plan. Line 2 converted to a control in laminar flow, Dec. 24, 1991 (Day 14 of the test run). All other cases and previous work are in turbulent flow as for line 3, control.

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Table 3: Analysis of Soluble Lactate and Acetate in Line 4 versus Control (Line 3)			
		Lactate (mg/l)	Acetate (mg/l)
Day	Line		
Day 1	3 Control	1.5	3.0, 7[1]
	4 + acetate, lactate	<0.5	5.5, 5[1,2]
Day 12	3 Control	<0.5	<0.1, 7[1]
	4 + acetate, lactate	<0.5	<0.2, 1[1]
Day 43	3 Control	<0.5	<0.2, <0.5[1]
	4 + acetate, lactate	<0.5	<0.2, <0.5[1,2]
Day 64	4 + acetate, lactate	95	120, 249[1]
Day 70	3 Control	<0.5	3.7, 8[1]
	4 + acetate, lactate	1.2	14.4, 86[1]

1. Second set of analysis performed by NHRC Analytical group.
2. Chemical injection pump on line 4 was not operating on these dates.

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Table 4: Corrosion Rates by Weight Loss Coupon and Potentiodyne Measurement					
CORROSION RATES (mm/year)					
	POTENTIODYNE			WEIGHT LOSS COUPONS	
	DAY 0	DAY 51	DAY 64	DAY 0	DAY 70
Line 1, + nitrate	0.0089	33	8.9	0.0017	0.776
Line 2, control - laminar flow	0.013	0.15	3.4	0.0016	0.085
Line 3, control - turbulent flow	0.014 0.017[1]	1.7	2.5	0.0022	0.121
Line 4, + acetate/lactate	0.15	1.4	2.9	0.0028	0.119
Line 5, + oxygen scavenger	0.014	1.5	3.2	0.018	0.126

1. using new probe tips freshly installed.

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Table 5: DNA Whole Genome Probe Assay for the Presence of Two Lactate (Lac4, Lac6) One Acetate (ACE1) and One Benzoate (Ben1) Utilizing Sulfate Reducing Bacteria in Biofilms				
SAMPLE	**ORGANISM**			
	ACE 1	**LAC 4**	**LAC 6**	**BEN 1**
Line 3 Control	-	-	-	-
Line 1 + Nitrate	+/-	-	+/-	-
Line 4 + Acetate/Lactate	+	+	+	+/-

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10.0 FIGURES

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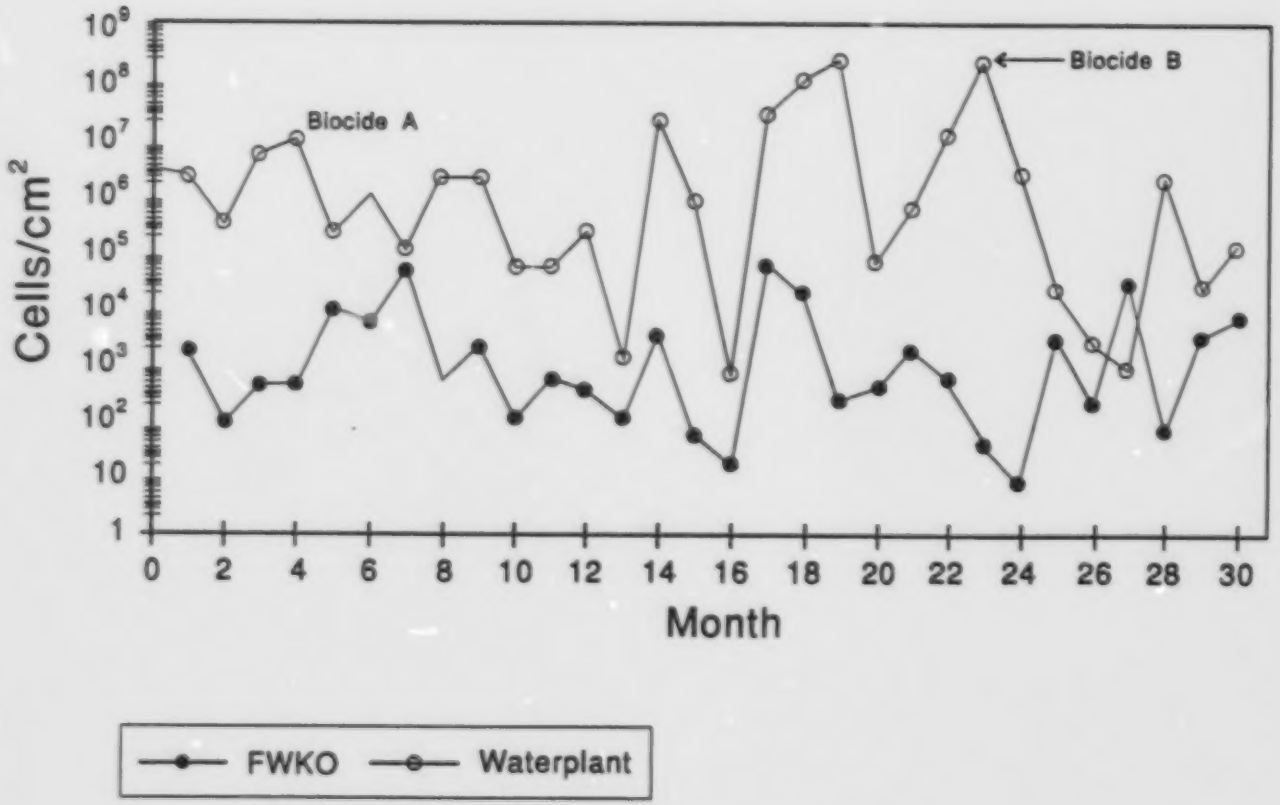
Figure 1: Field performance of Biocides A and then B showing level of control attainable and importance of other factors influencing bacterial numbers



FWKO - Free Water Knock Out - upstream of biocide injection
WATERPLANT - downstream of biocide injection

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Figure 2: Schematic diagram of water handling facility in Wainwright oilfield

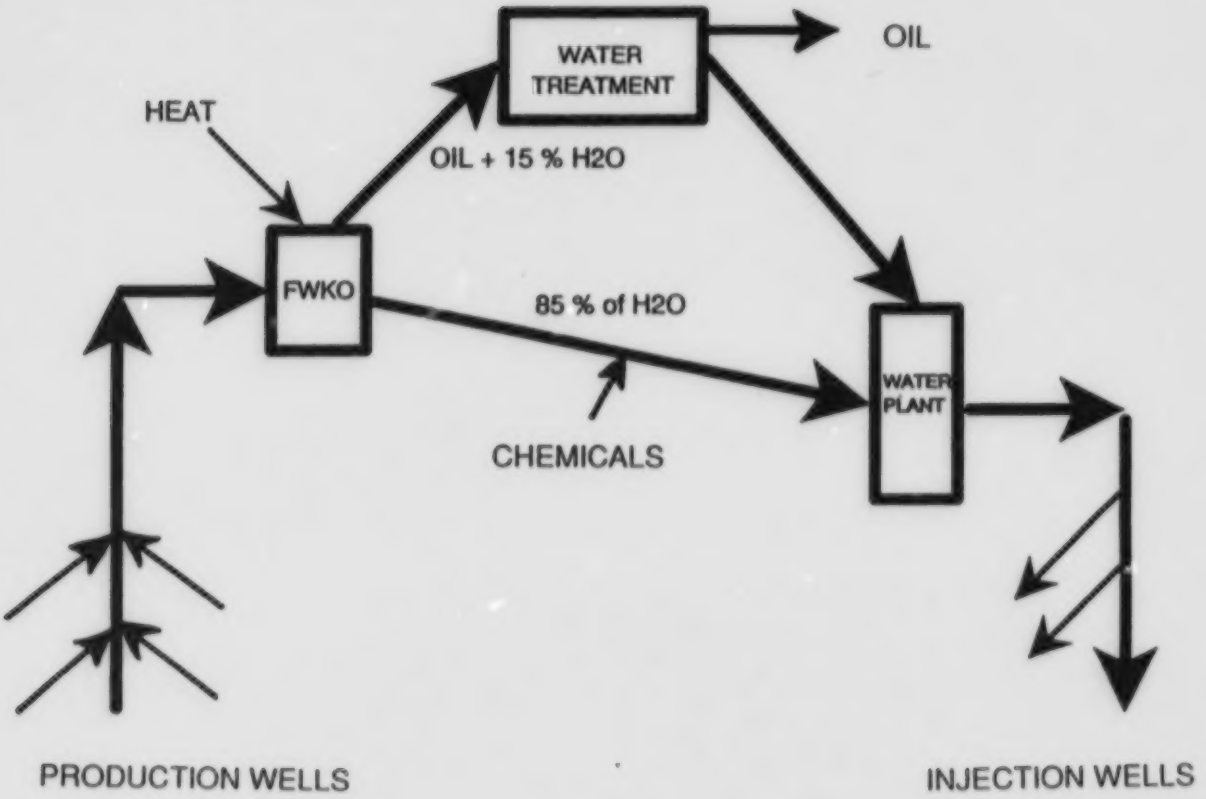

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Figure 3A: Relationship of soluble barium and sulfate at Free Water Knock Outs

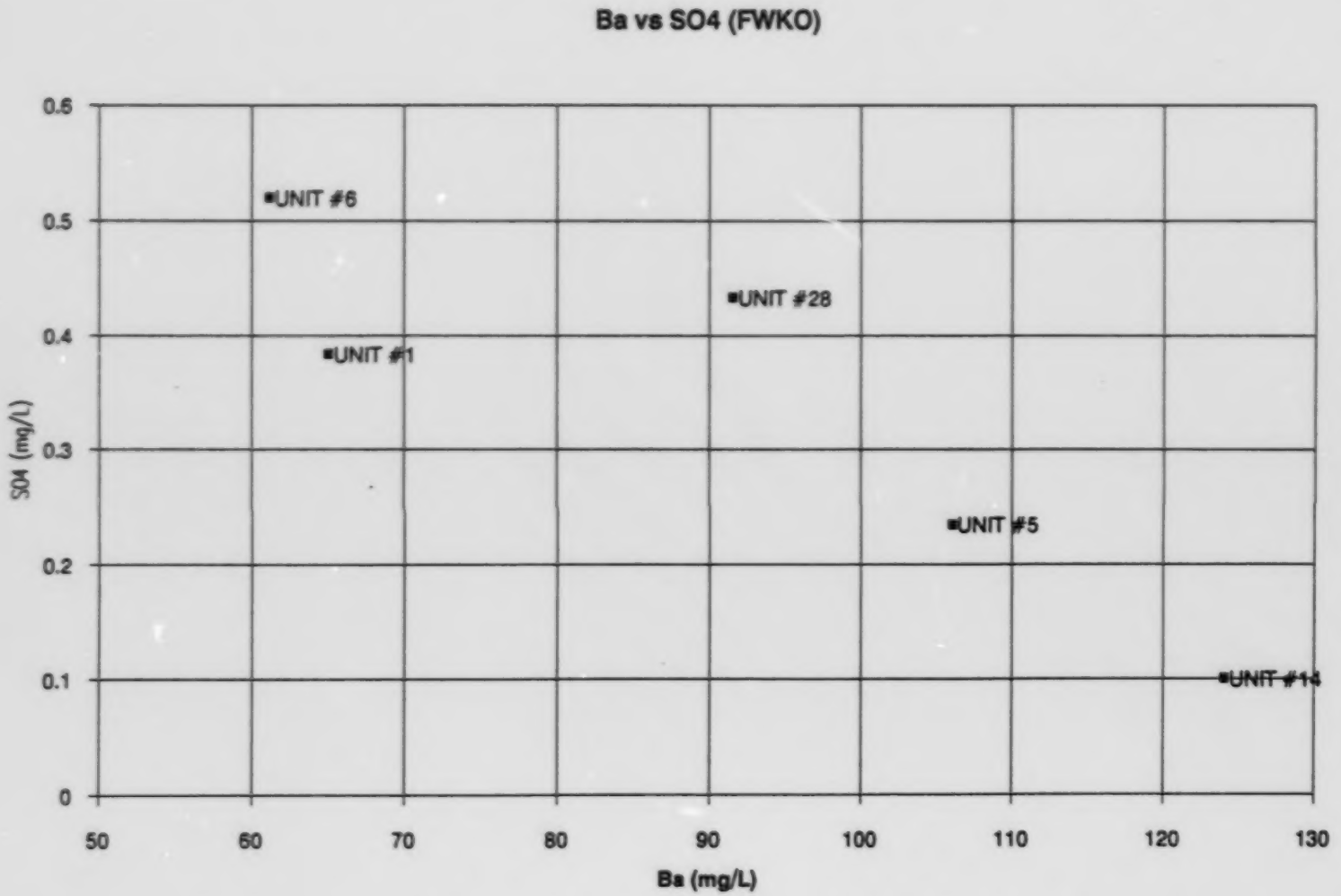

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Figure 3B: Relationship of soluble barium and sulfate at Waterplants

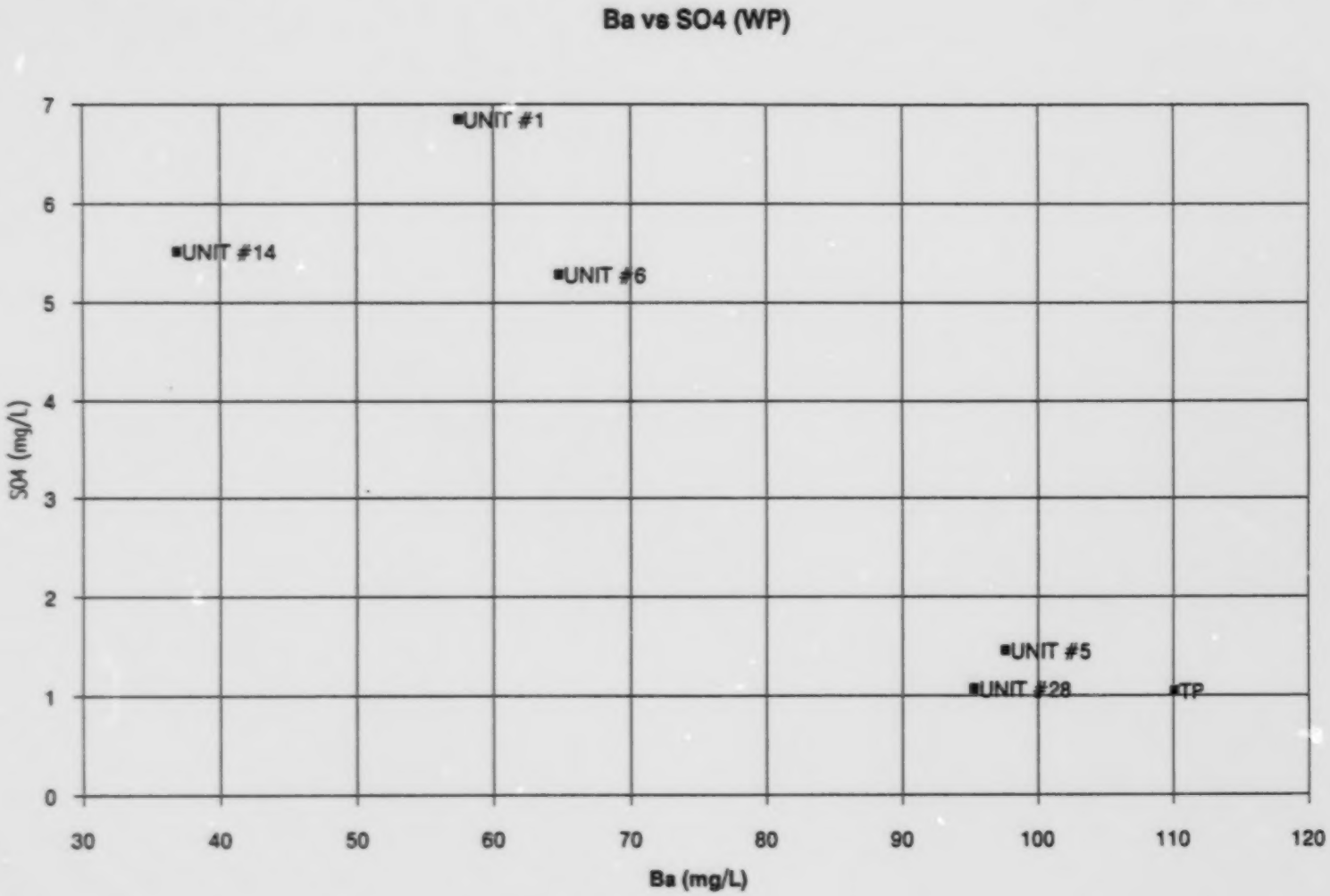

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Figure 4: Relative corrosion failure costs for various units over time

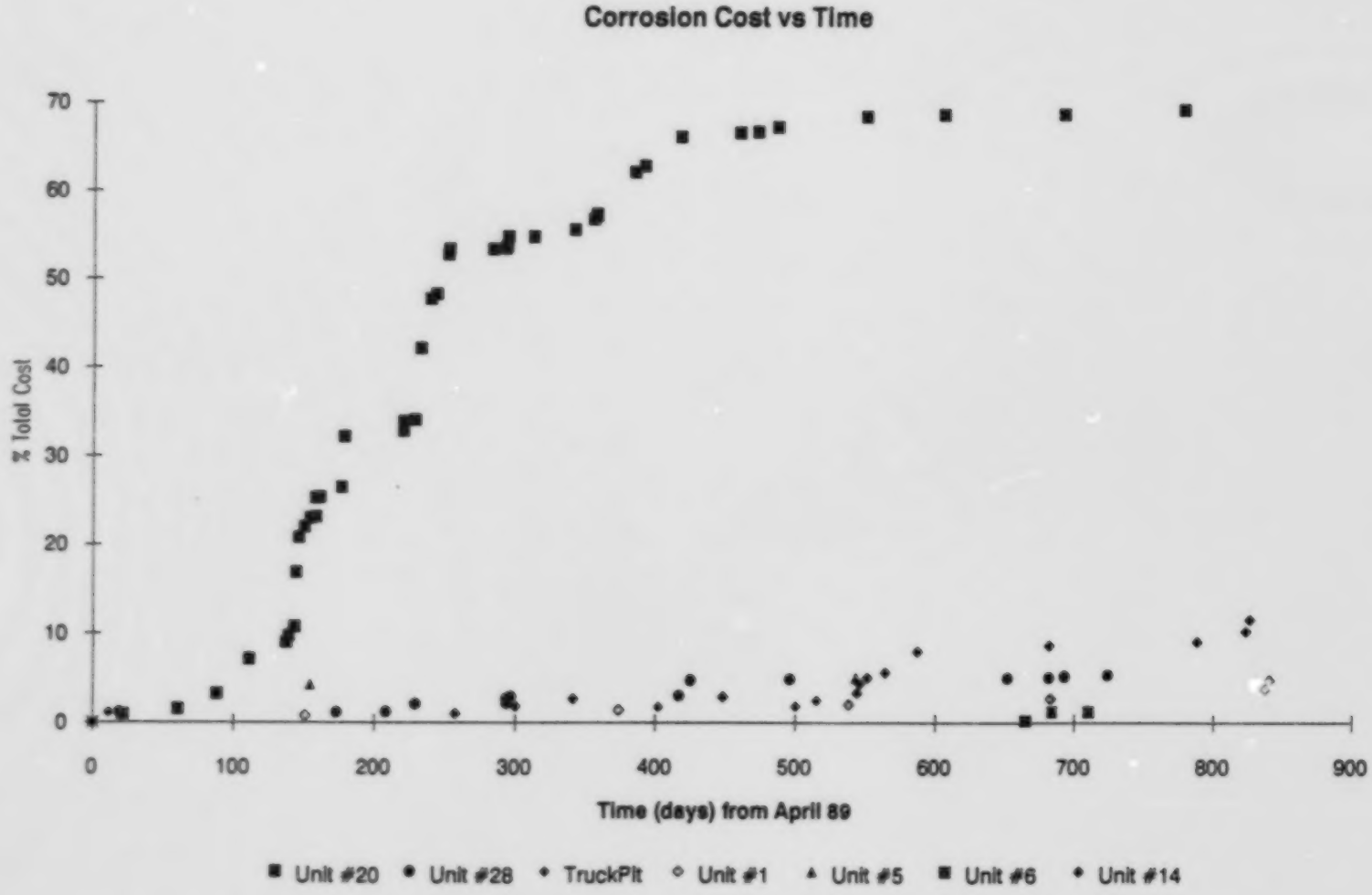

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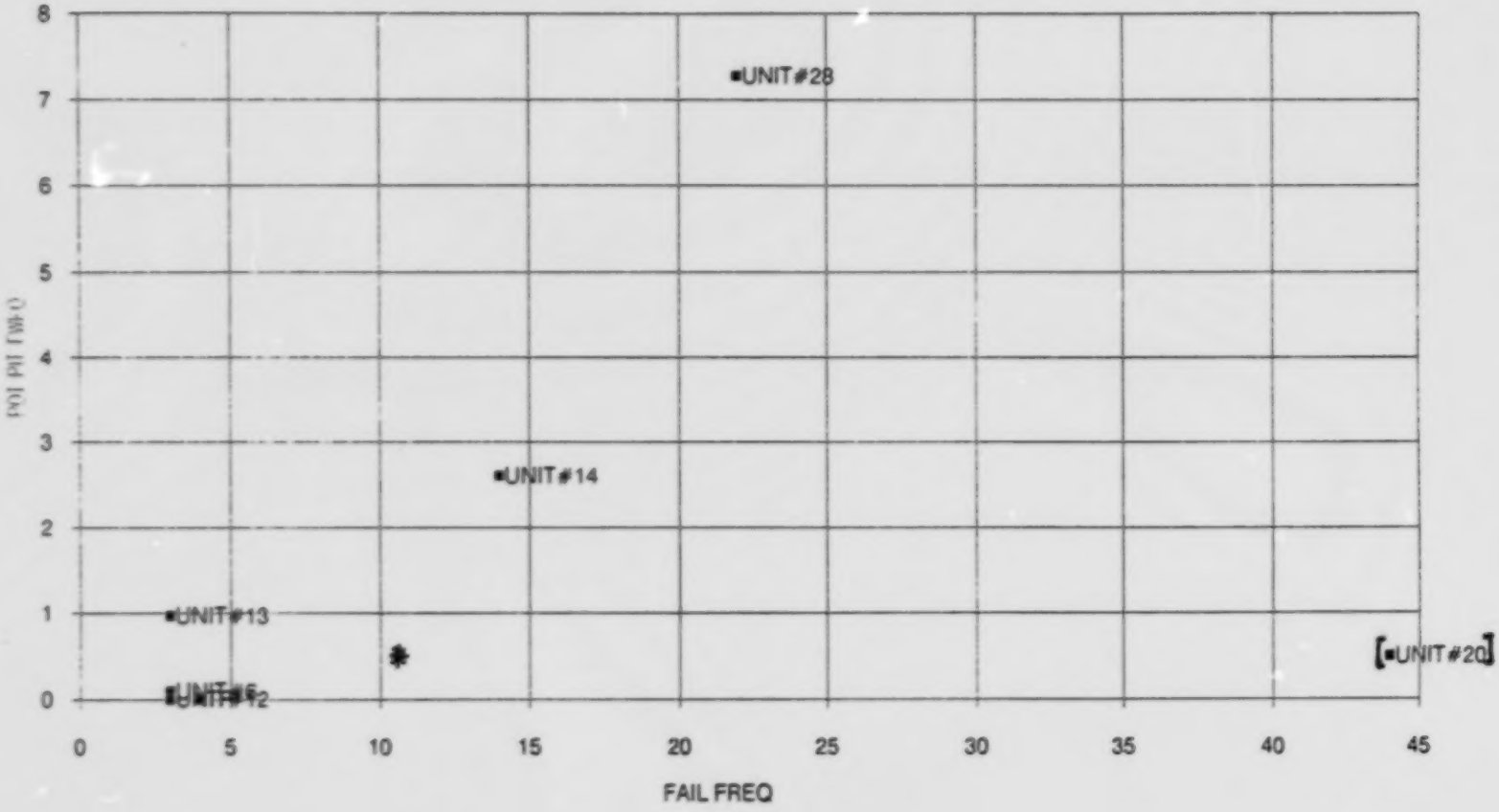
Figure 5: Correlation of potentiodyne pitting index at the Free Water Knock Out and frequency of failures



* CORRECTED VALUE FOR UNIT 20. Corrected for failure frequency observed after removal of truckpit water.

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Figure 6: Correlation of potentiodyne corrosion rates with weight loss coupon data

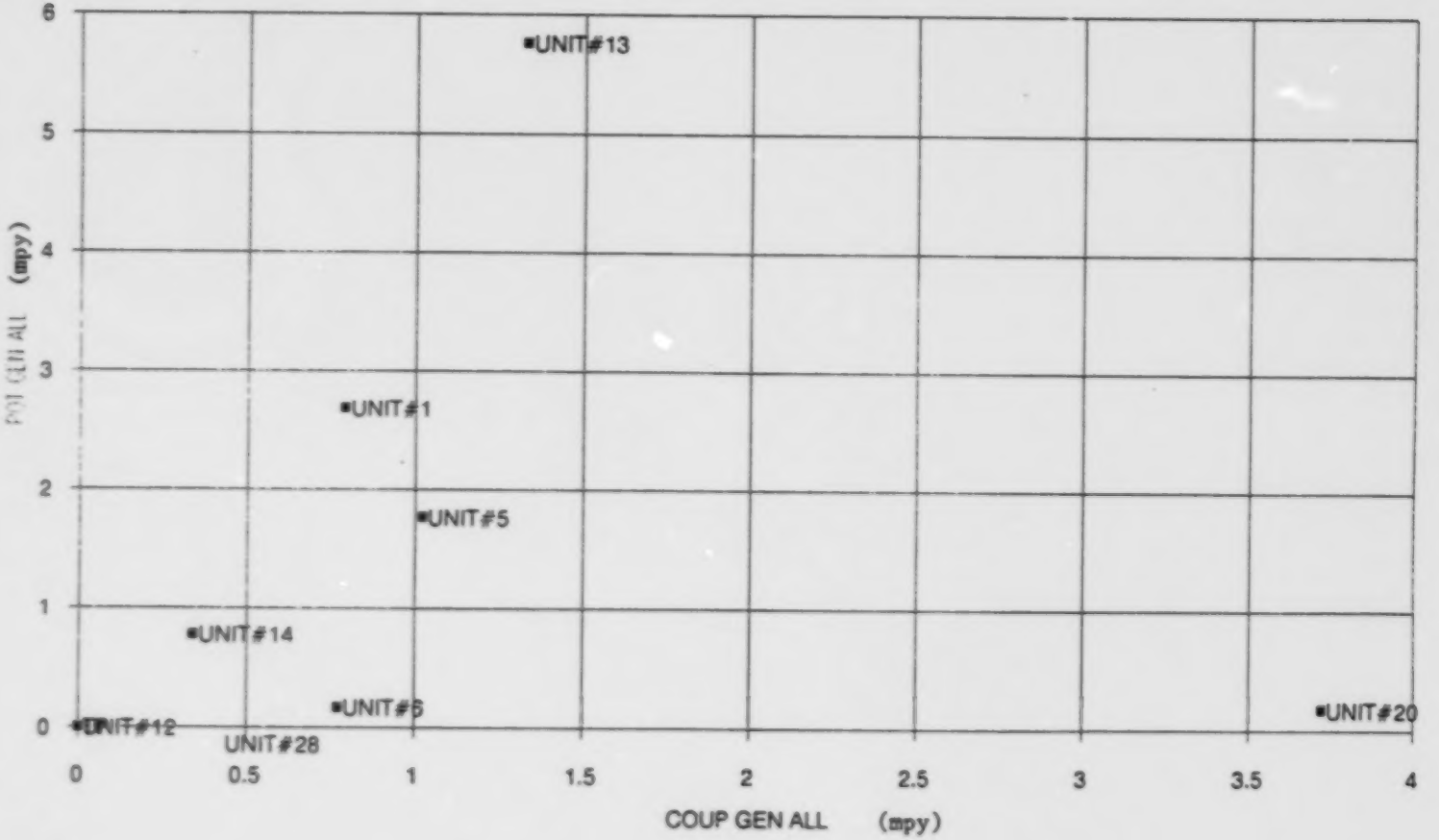

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Figure 7: Correlation of soluble manganese and iron

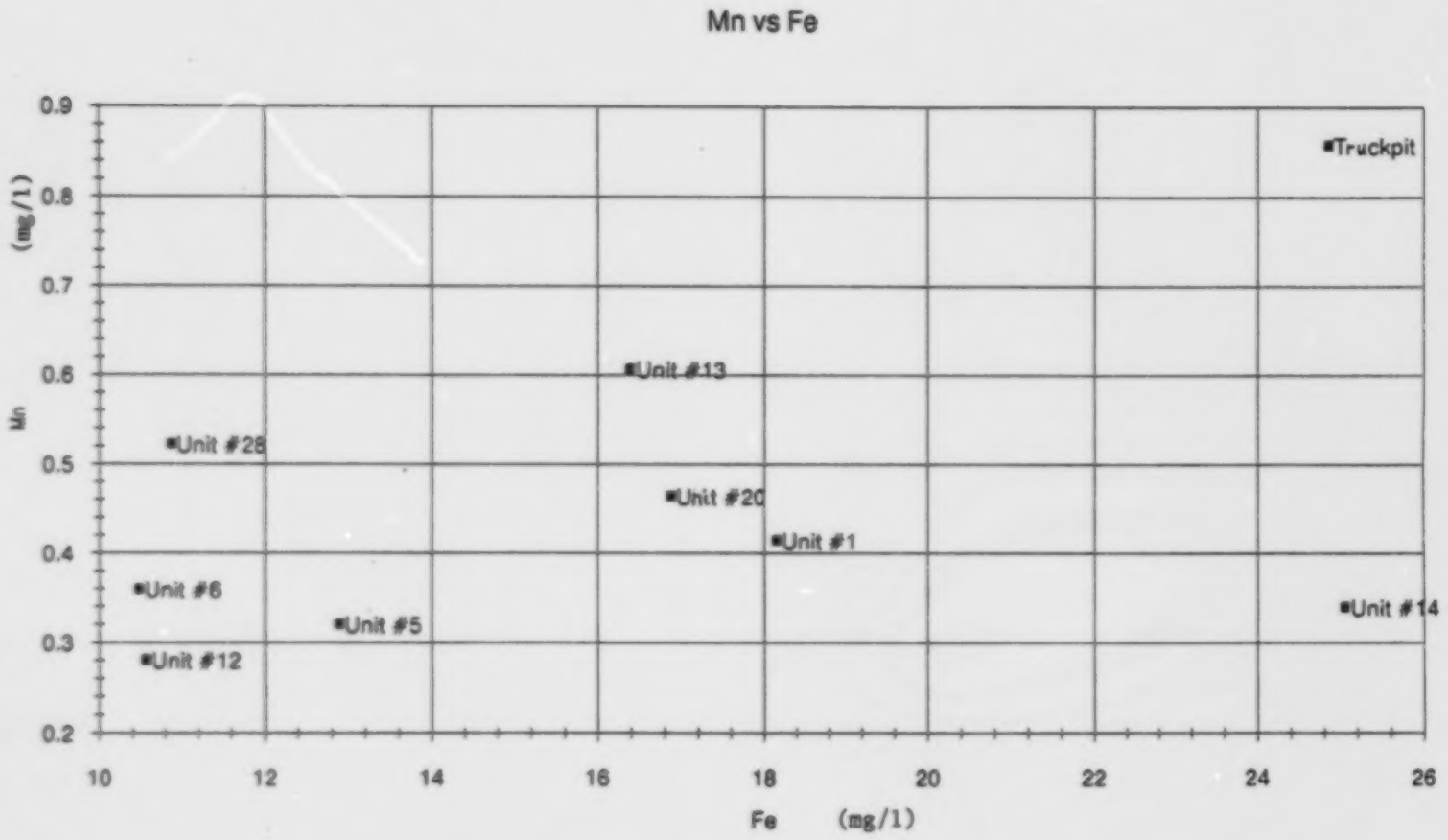

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Figure 8: Correlation of produced water conductivity at free water knock out and failure costs for unit

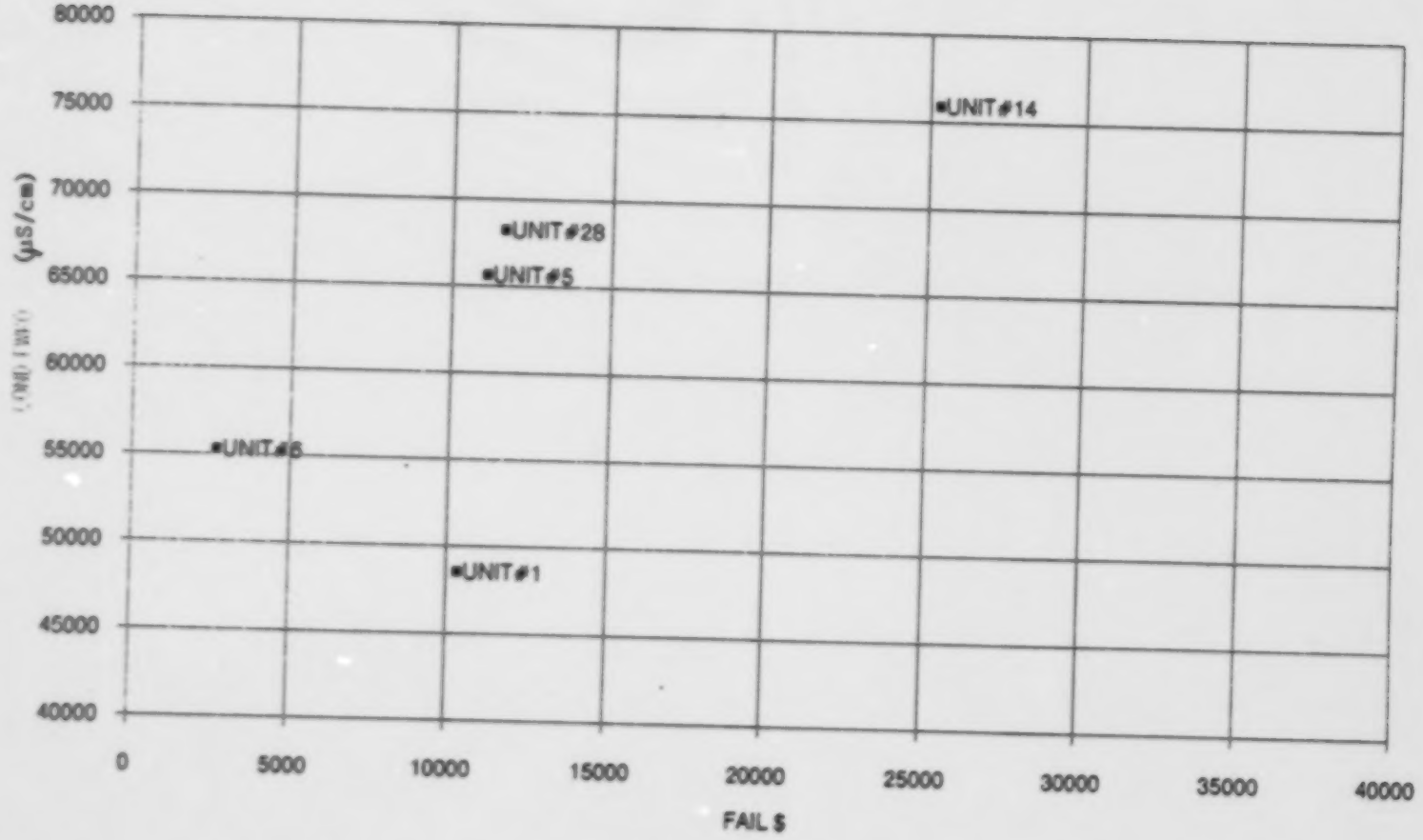

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Figure 9: Correlation of produced water hardness at free water knock out with cost of failures

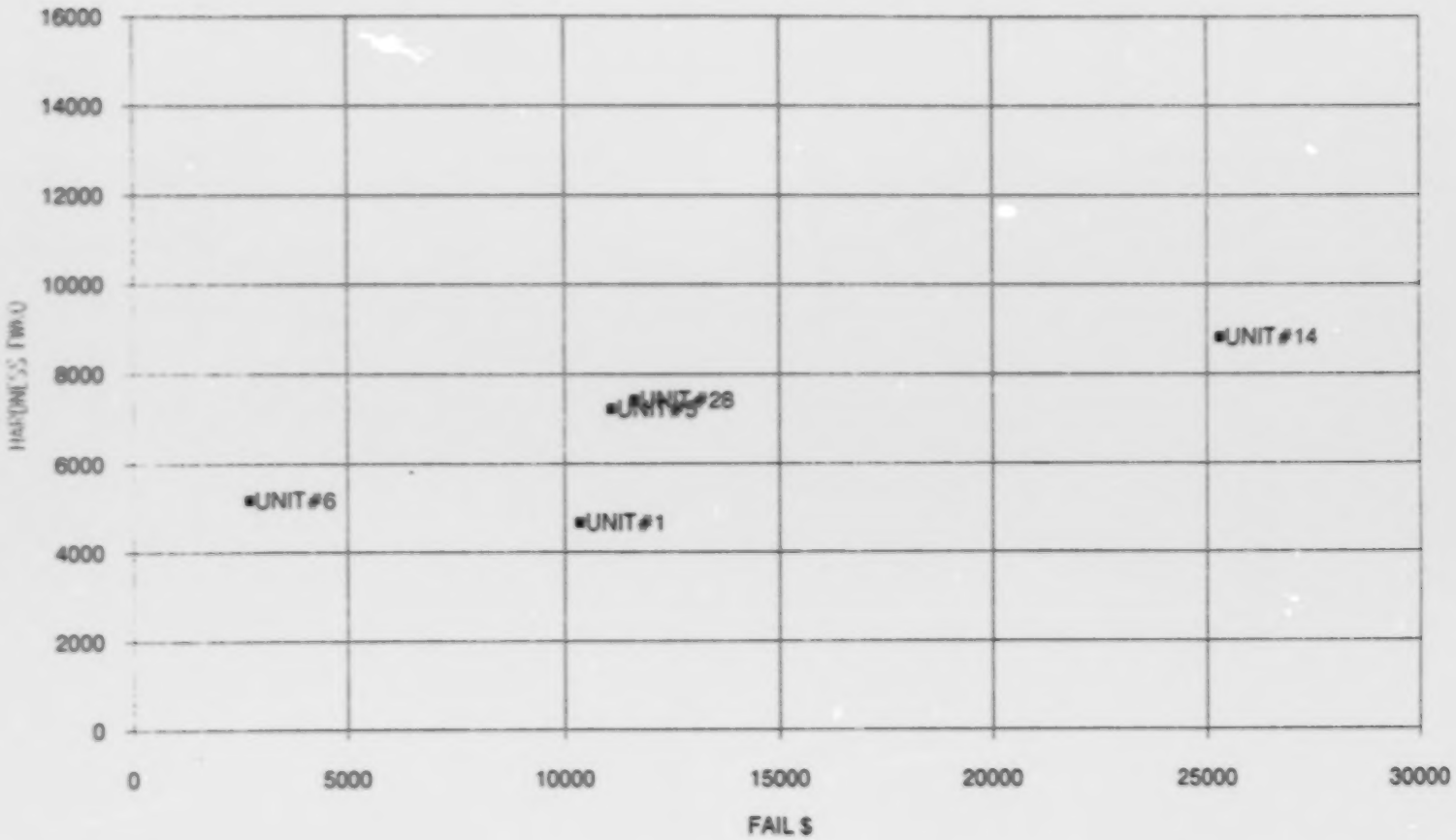

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Figure 10: Correlation of suspended solids with corrosion rate by potentiodyne

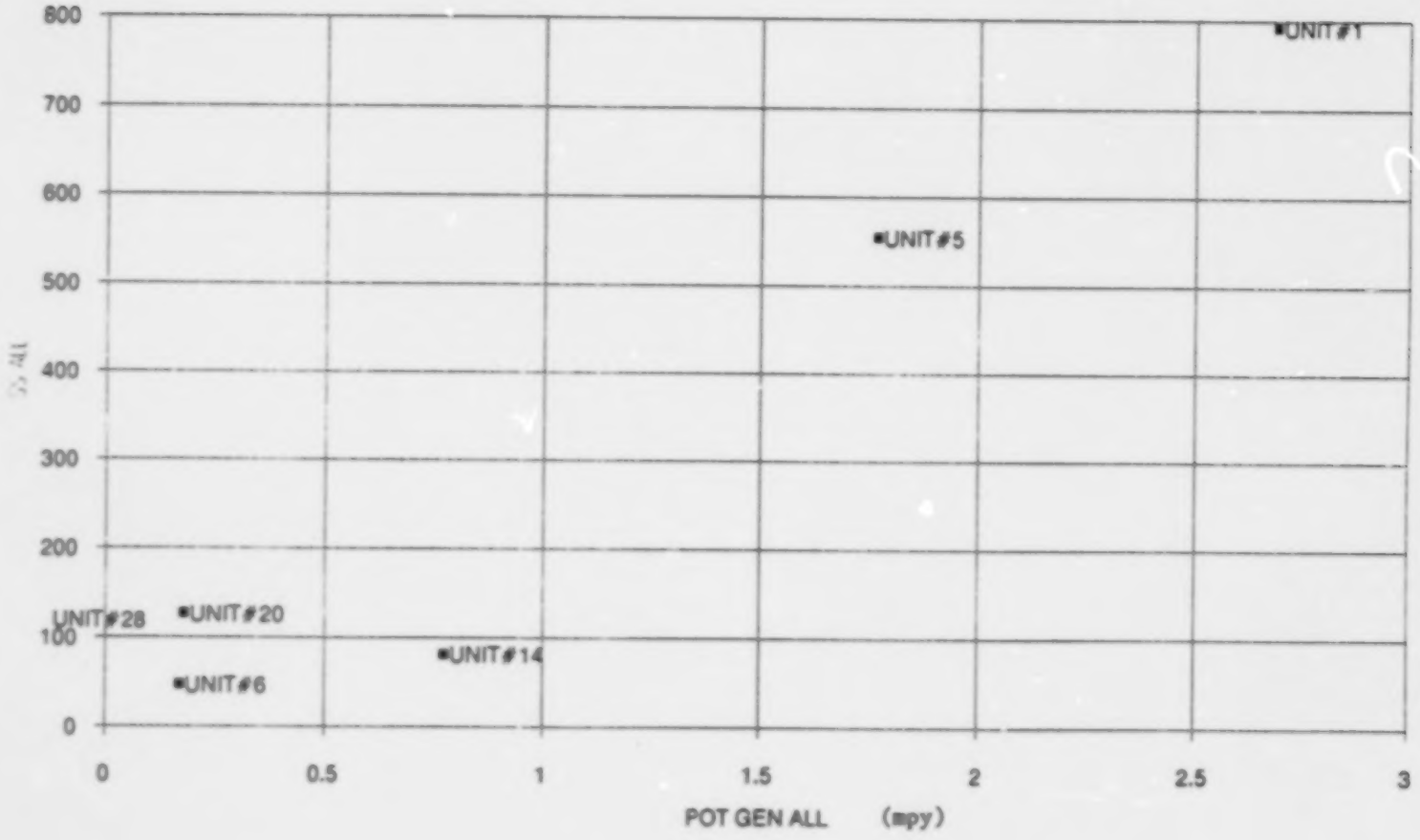

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Figure 11: Correlation of suspended solids with corrosion rate by weight loss coupons at free water knock out

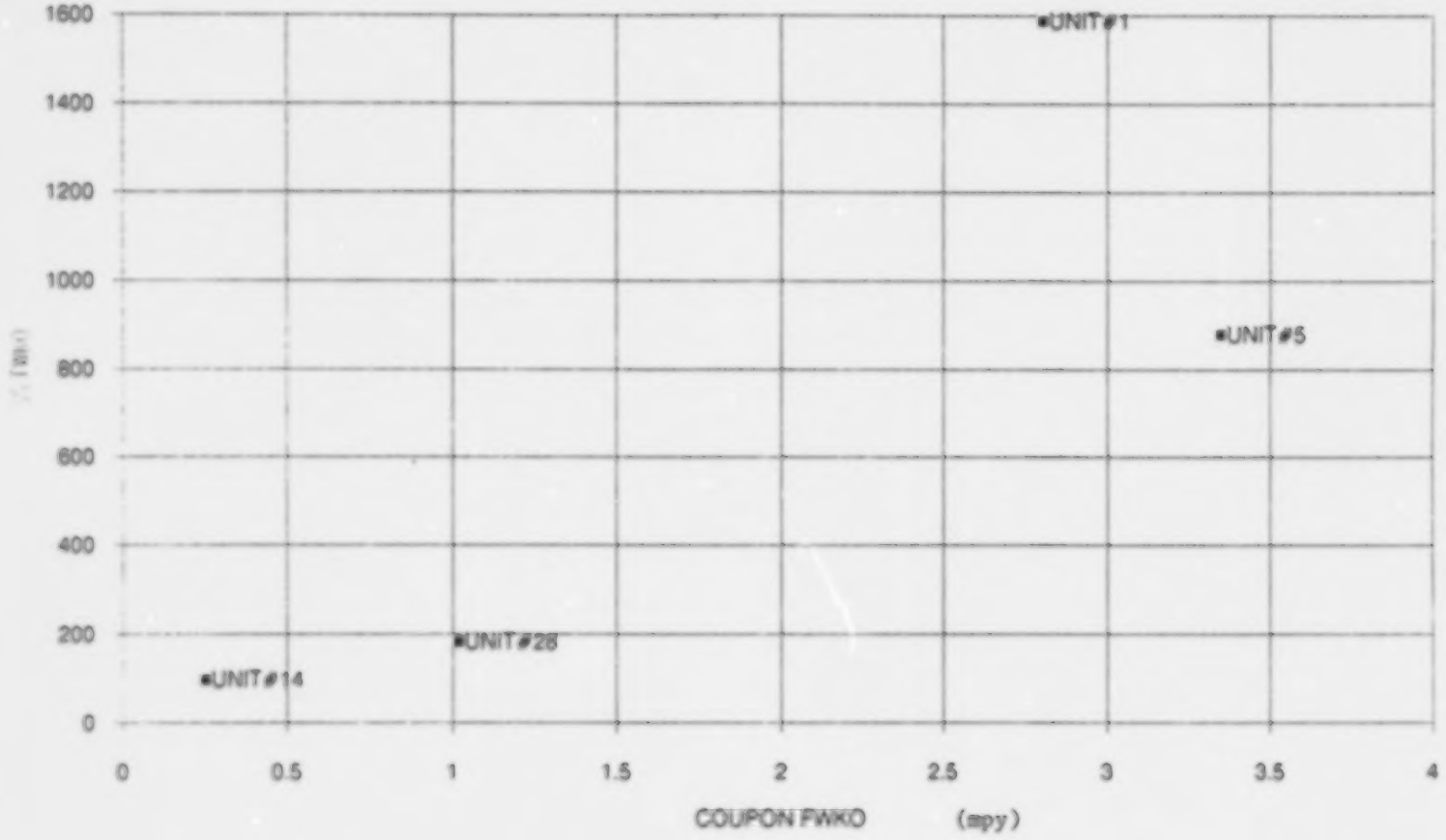

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Figure 12: Correlation of oil and grease with cost of failures

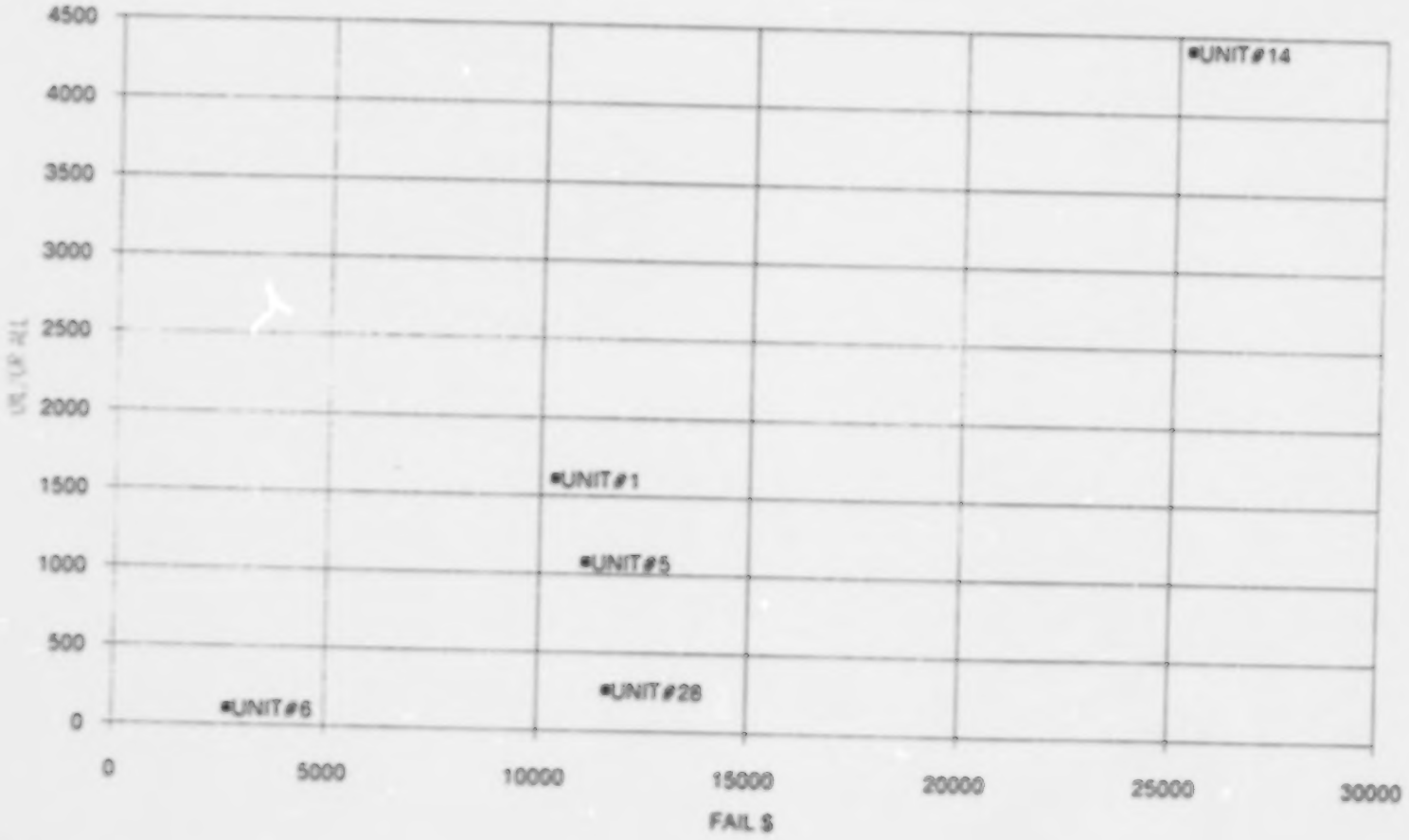

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Figure 13: Correlation of soluble sulfate with failure frequency

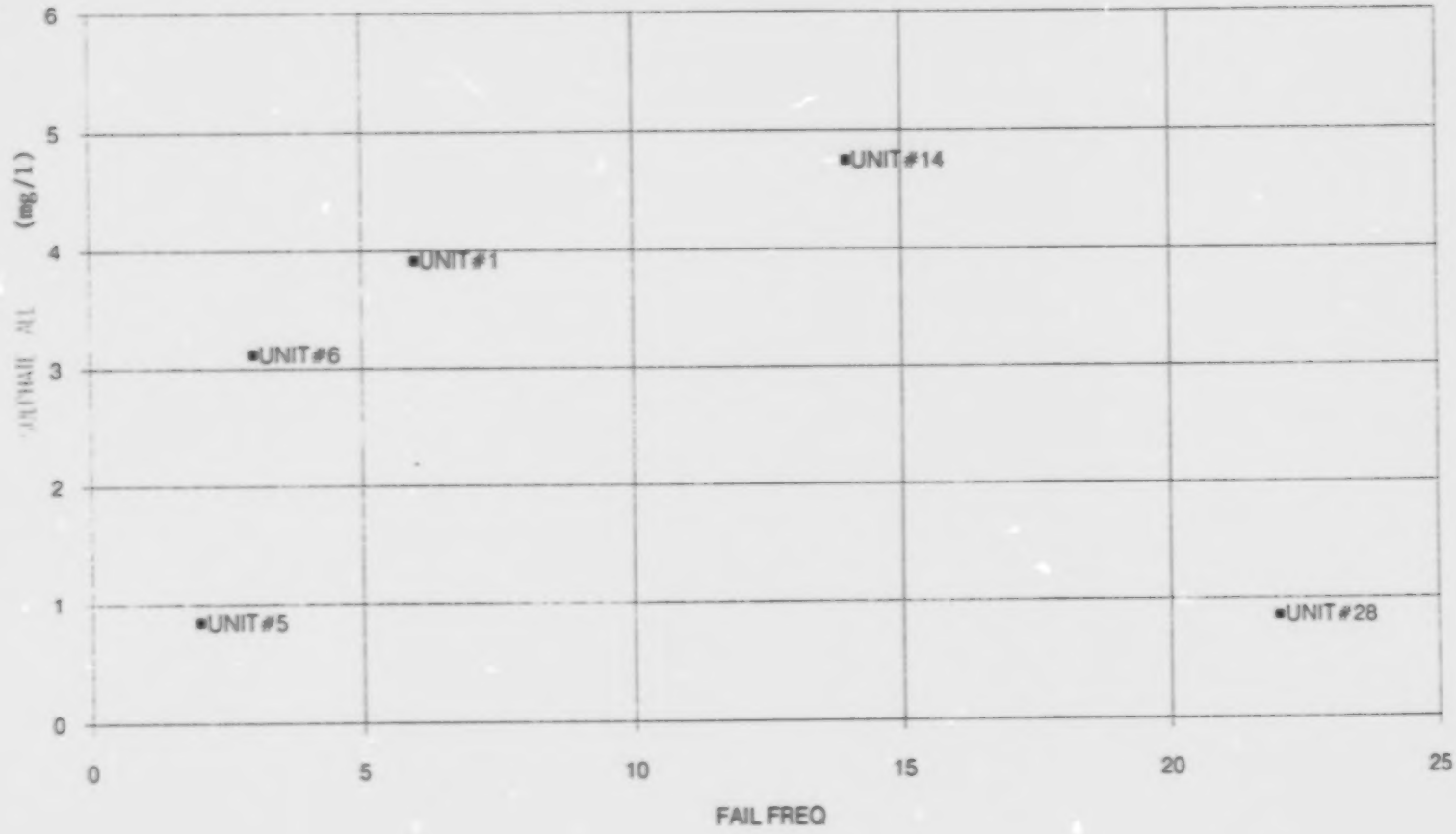

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Figure 14: Correlation of residual sulfite at waterplant with cost of failures

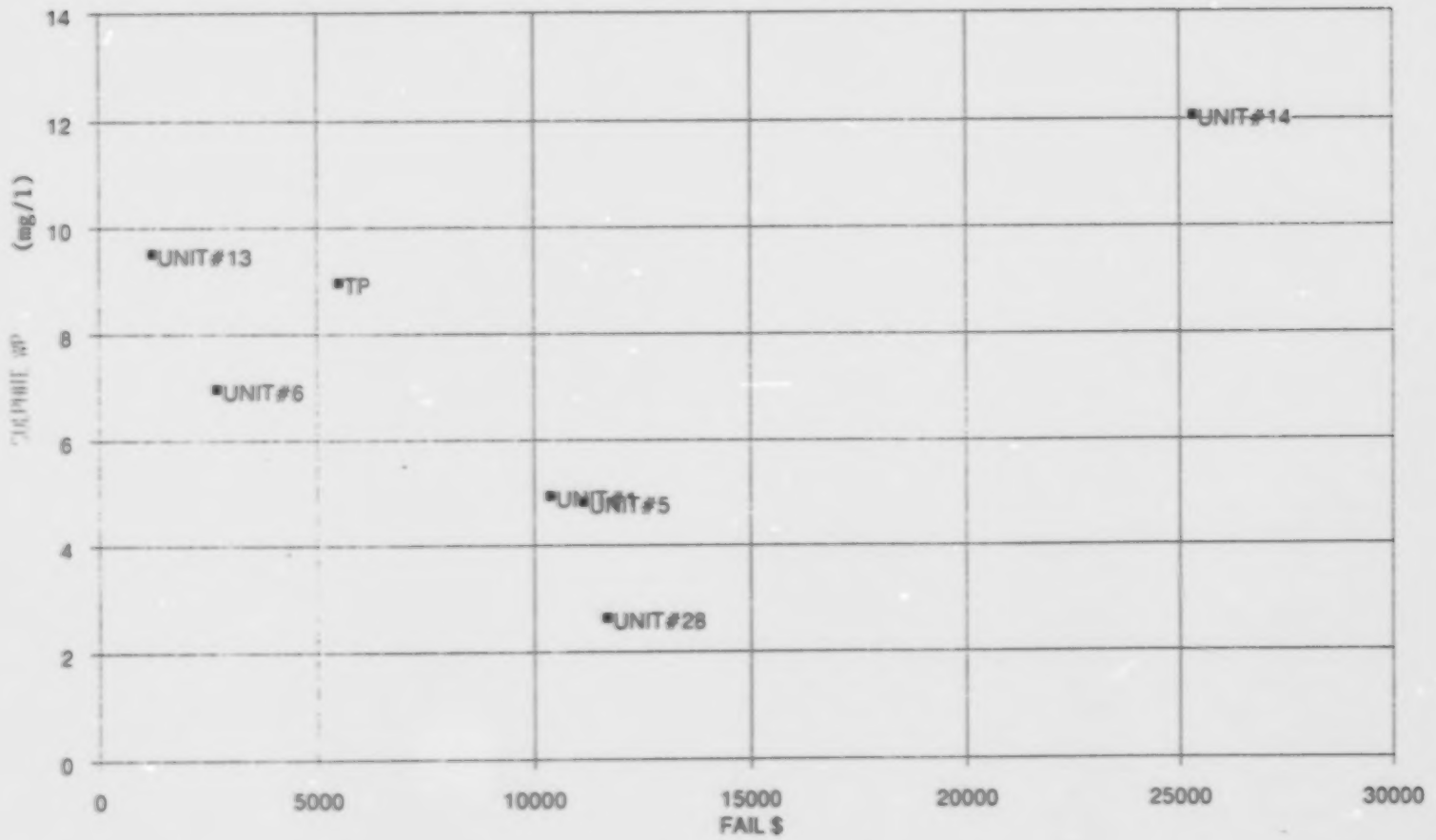

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Figure 15: Correlation of residual sulfite at waterplant with corrosion rate by weight loss coupon

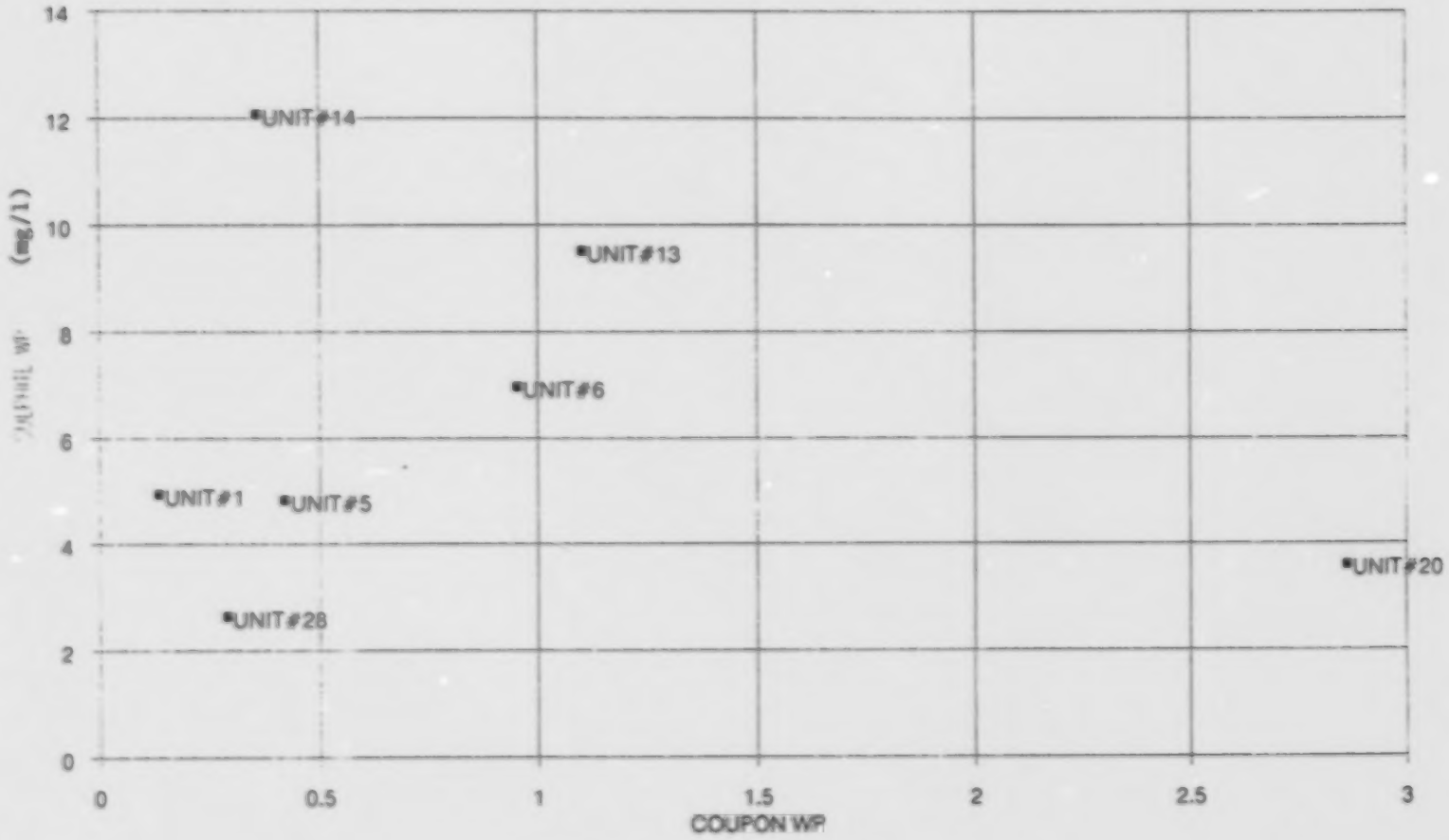

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Figure 16: Correlation of residual sulfite at waterplant with corrosion rate by potentiodyne

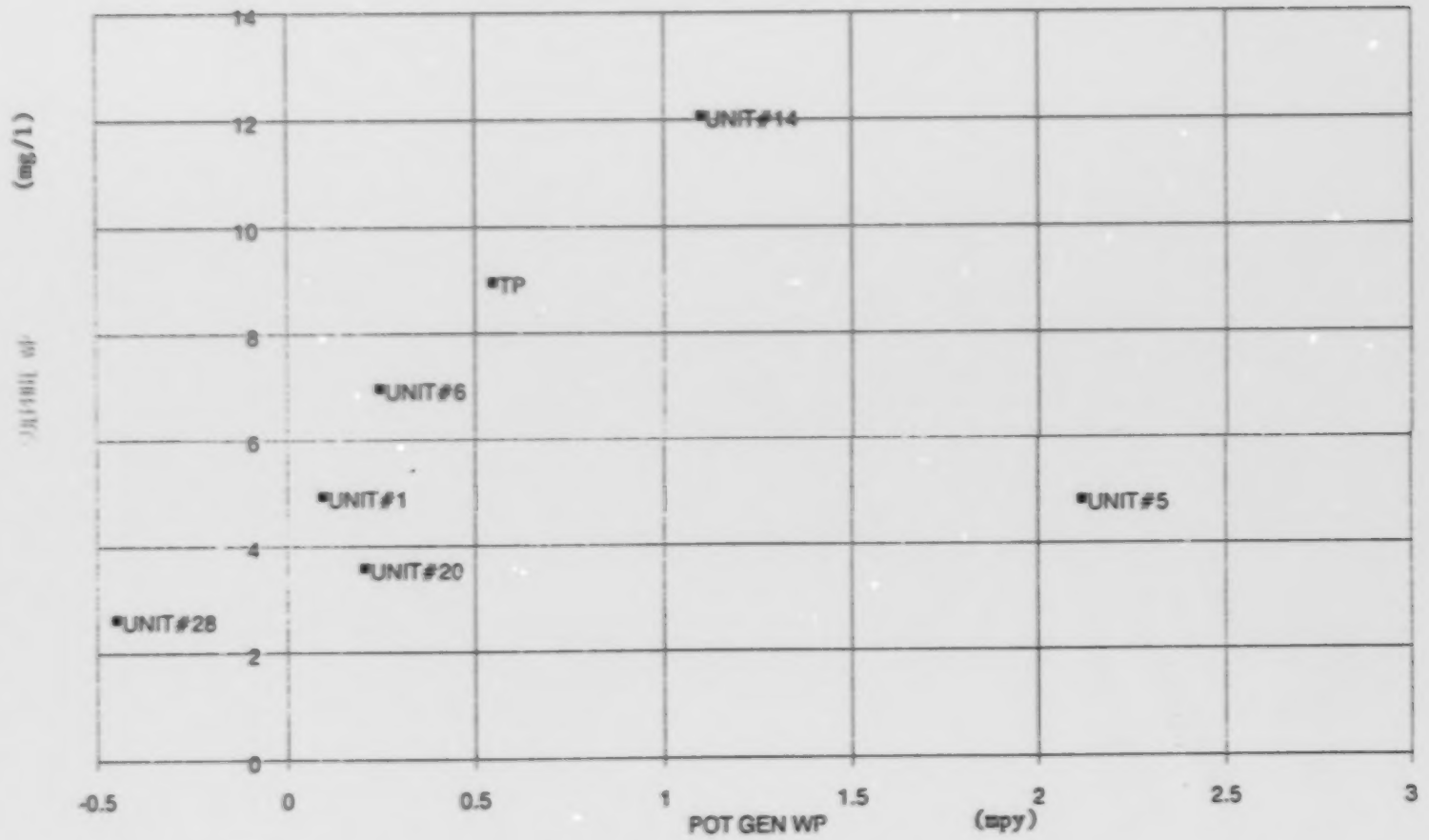

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Figure 17: Correlation of residual corrosion inhibitor with cost of failures

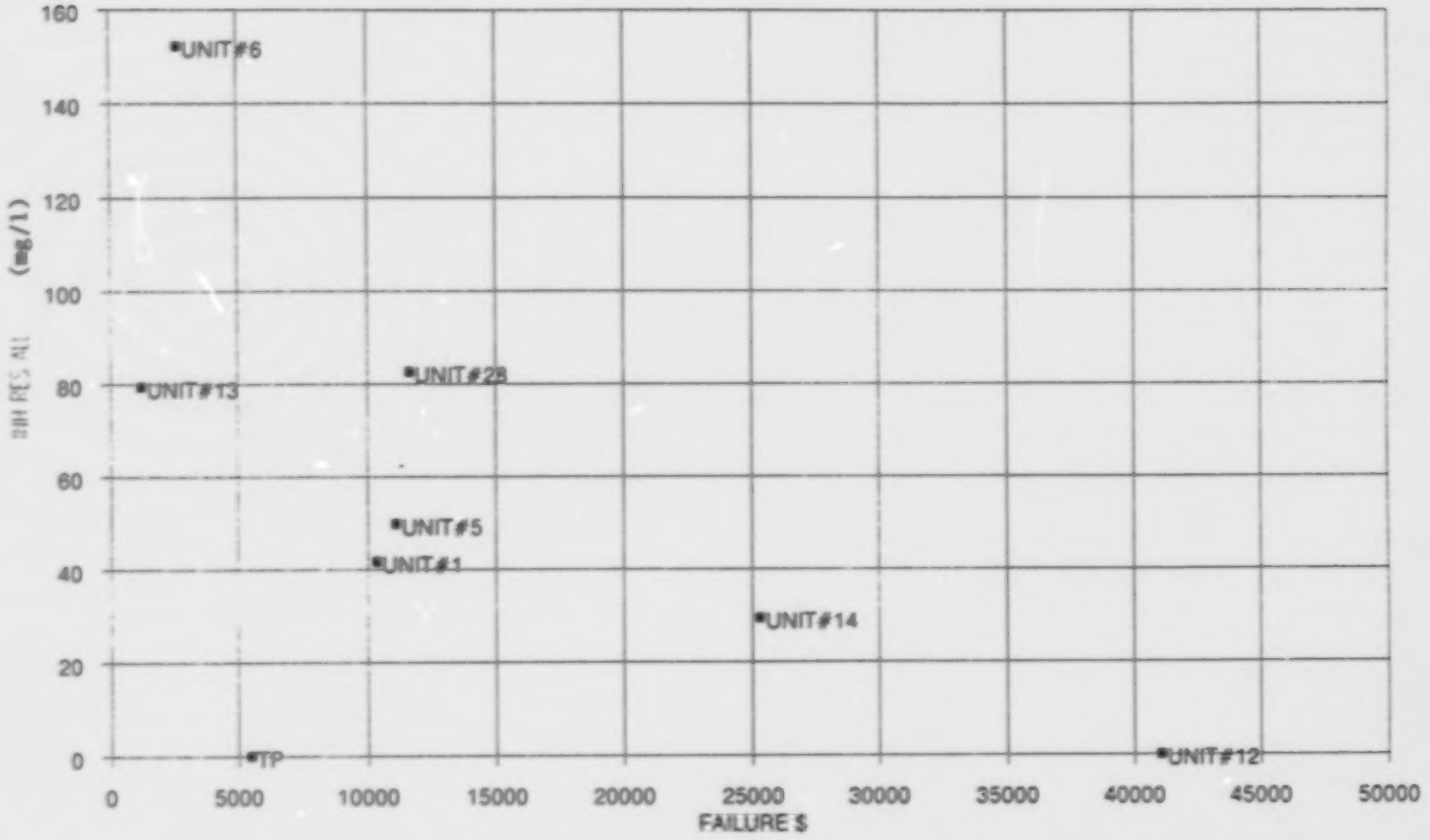

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Figure 18: Distributions of viable sulfate reducing bacteria (#/cm^2) in biofilm at Free Water Knock Out and Waterplant, Unit 1, over 30 month audit

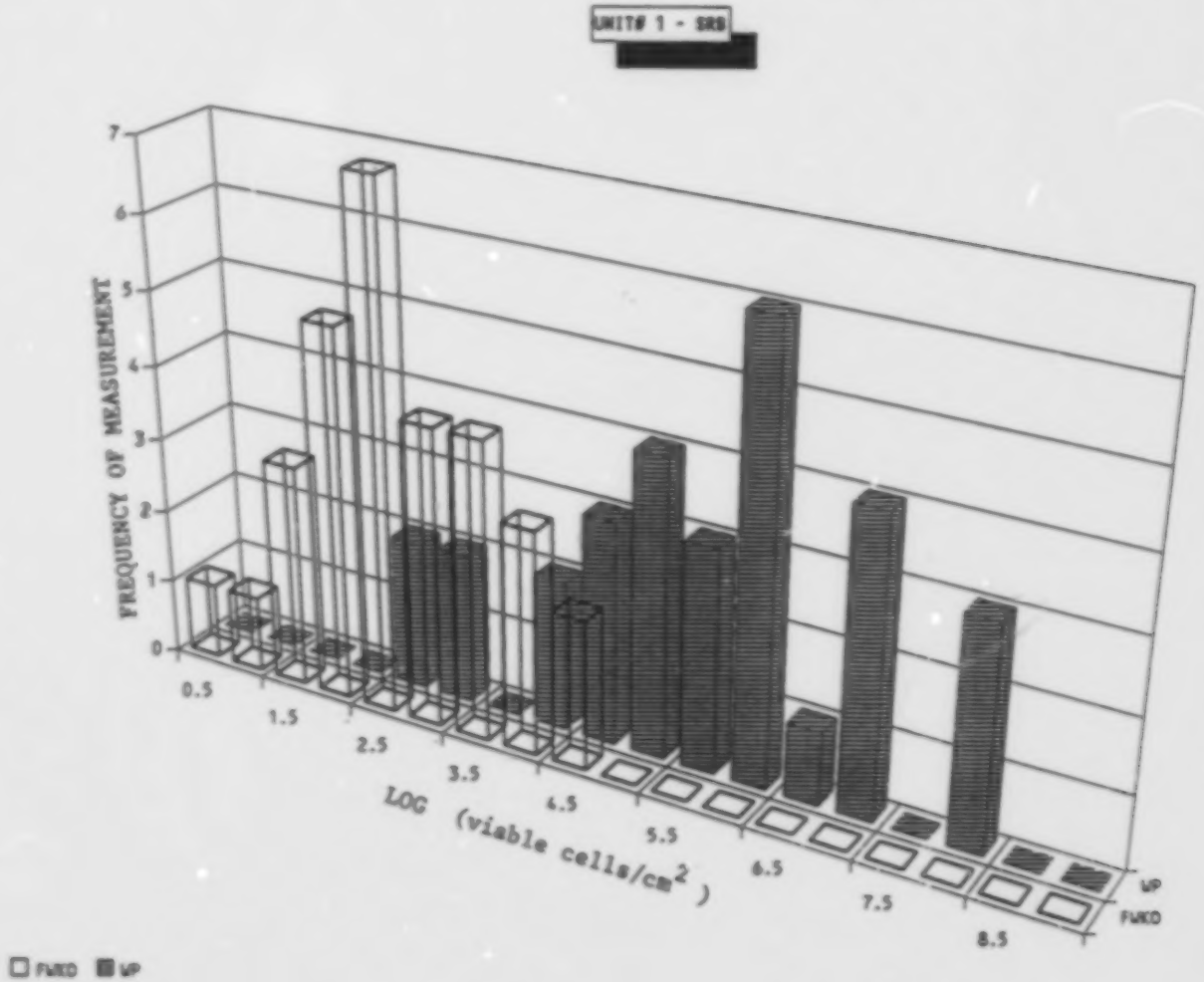

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Figure 19: Correlation of acid producing bacteria (APB) with sulfate reducing bacteria (SRB) in waterplant biofilms

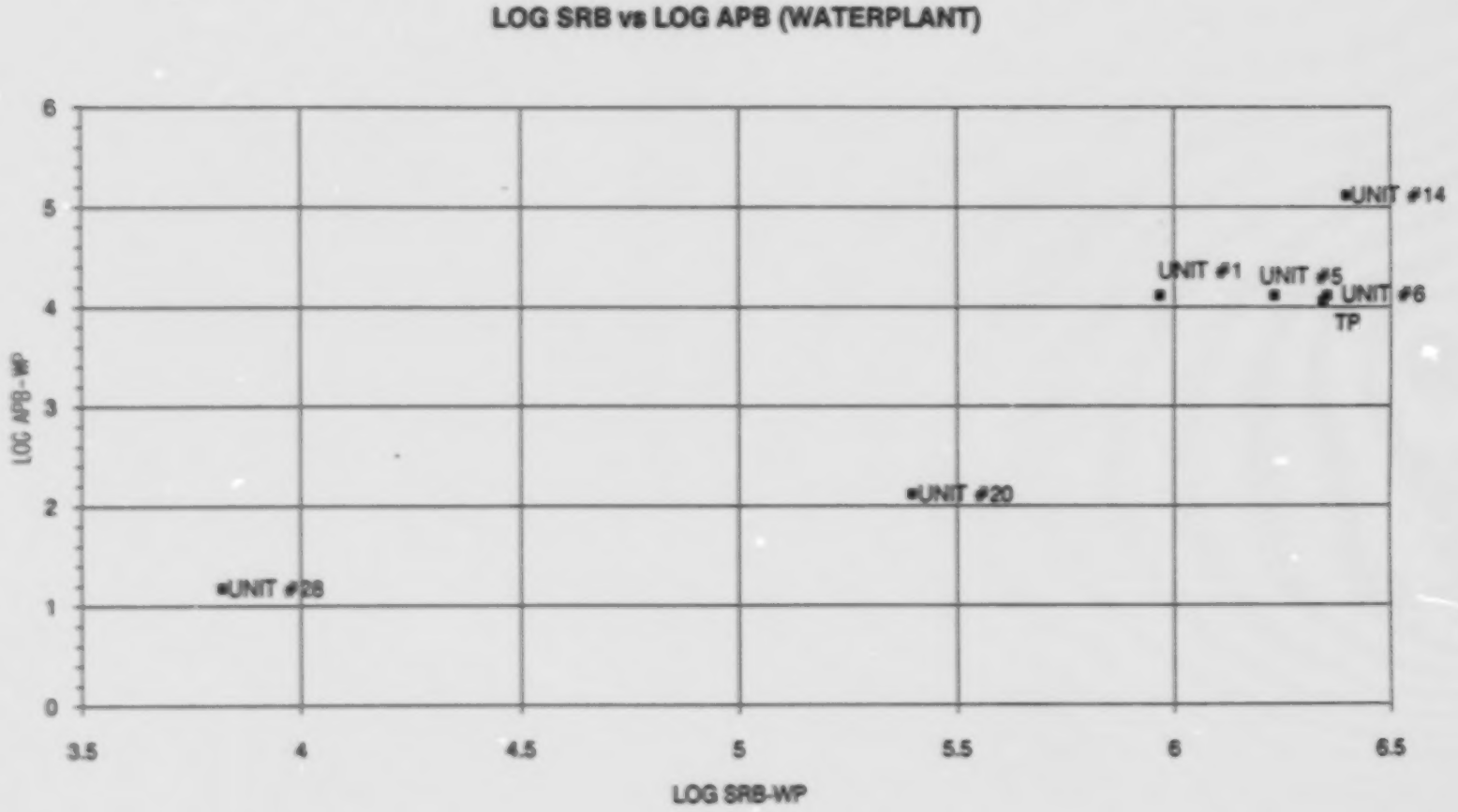

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Figure 20: Correlation between acid producing bacteria (APB) present and increase in sulfate reducing bacteria (SRB) (Free Water Knock Out to Waterplant)

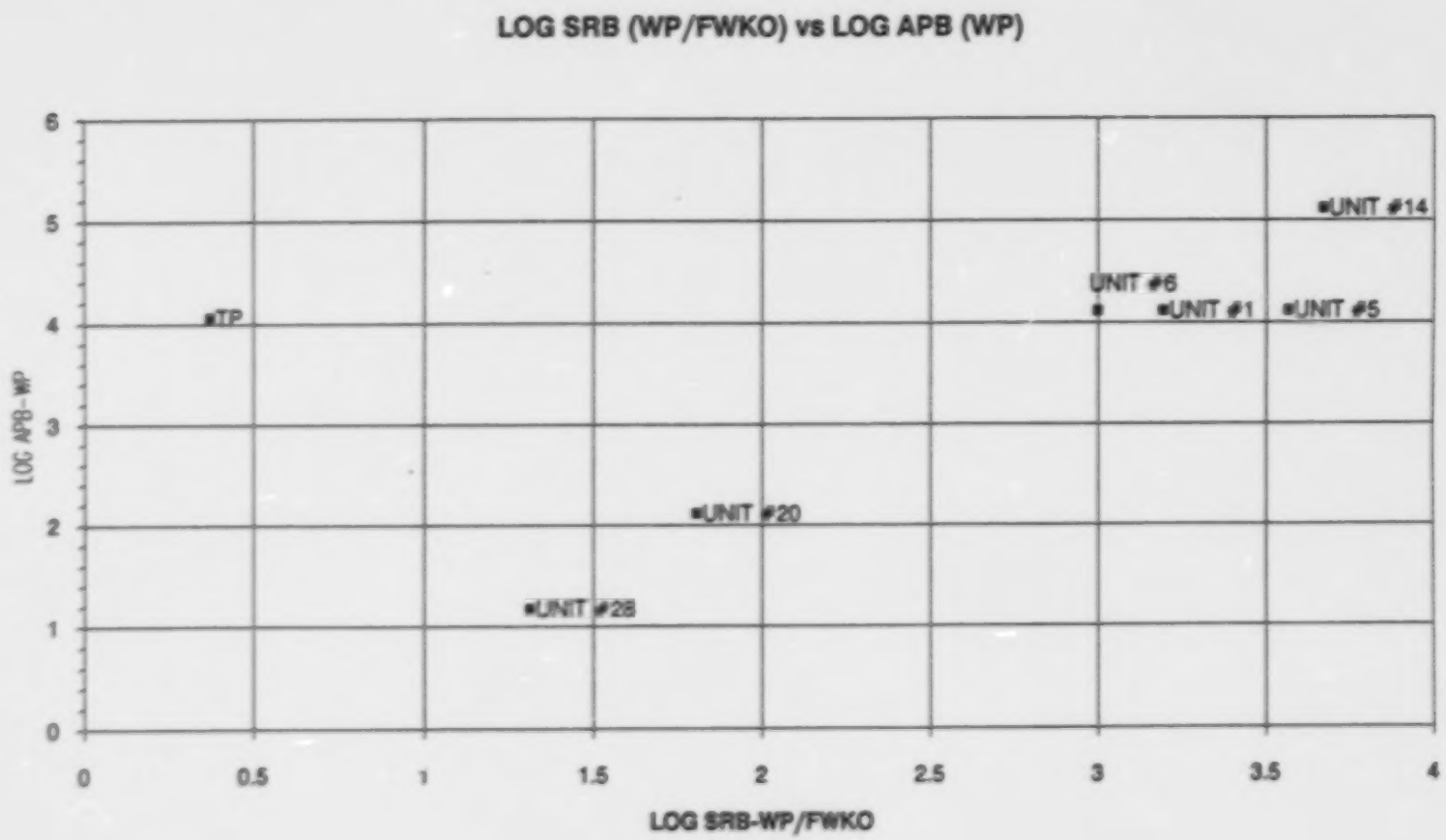

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Figure 21: Correlation between acid producing bacteria (APB) and increase in sulfate reducing bacteria (SRB) from free water knock out to waterplant, Unit 1

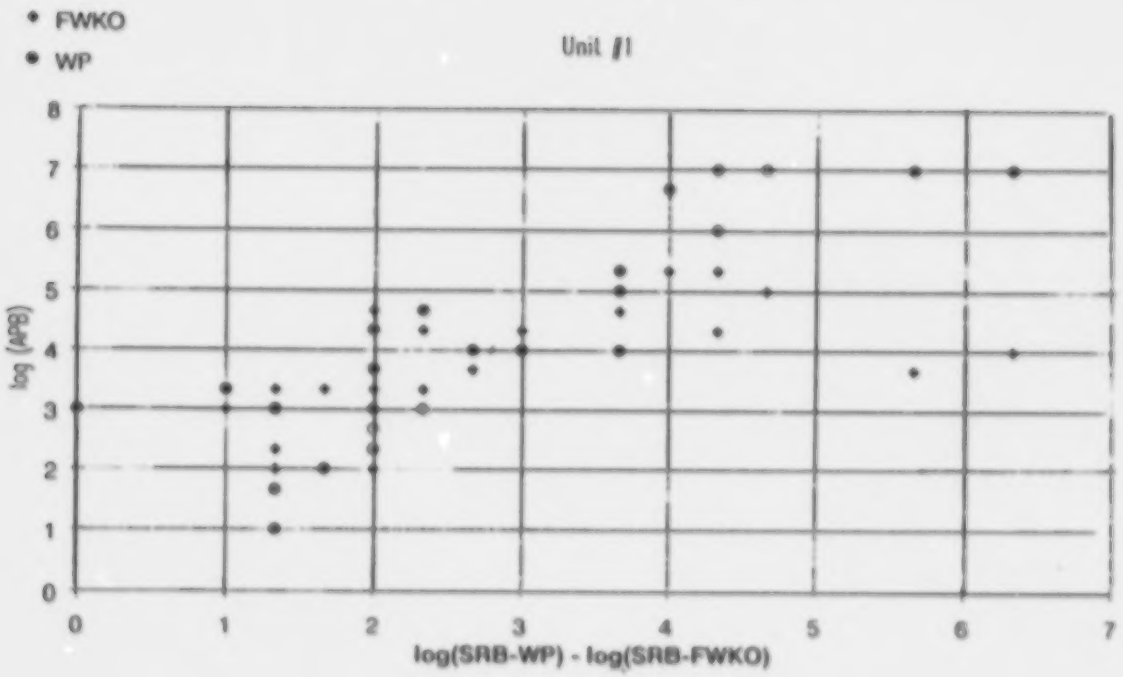

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Figure 22: Correlation between magnesium concentration and density of sulfate reducing bacteria (SRB) in waterplant biofilms

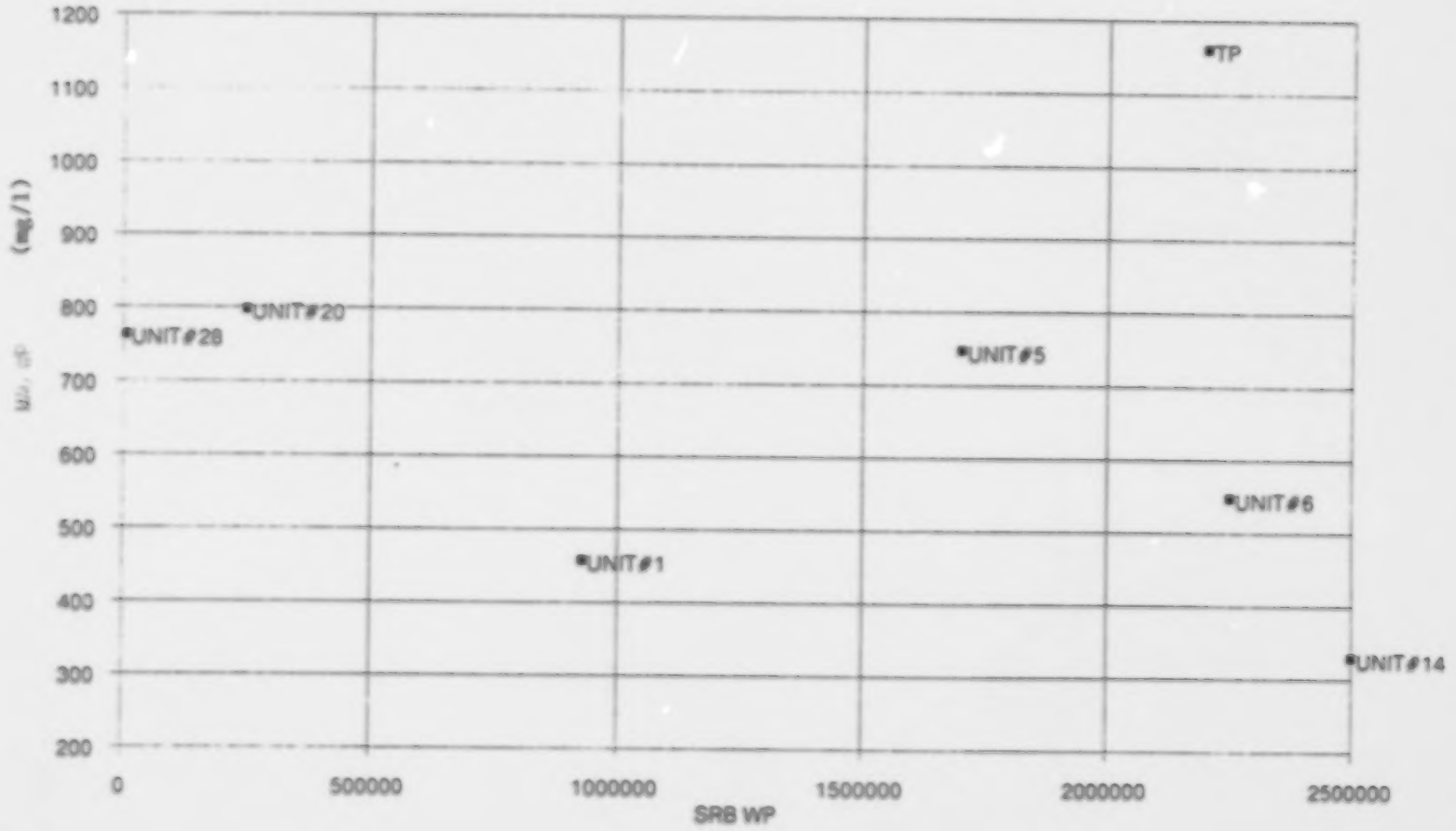

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Figure 23: Correlation of water hardness with density of acid producing bacteria (APB) in waterplant biofilms

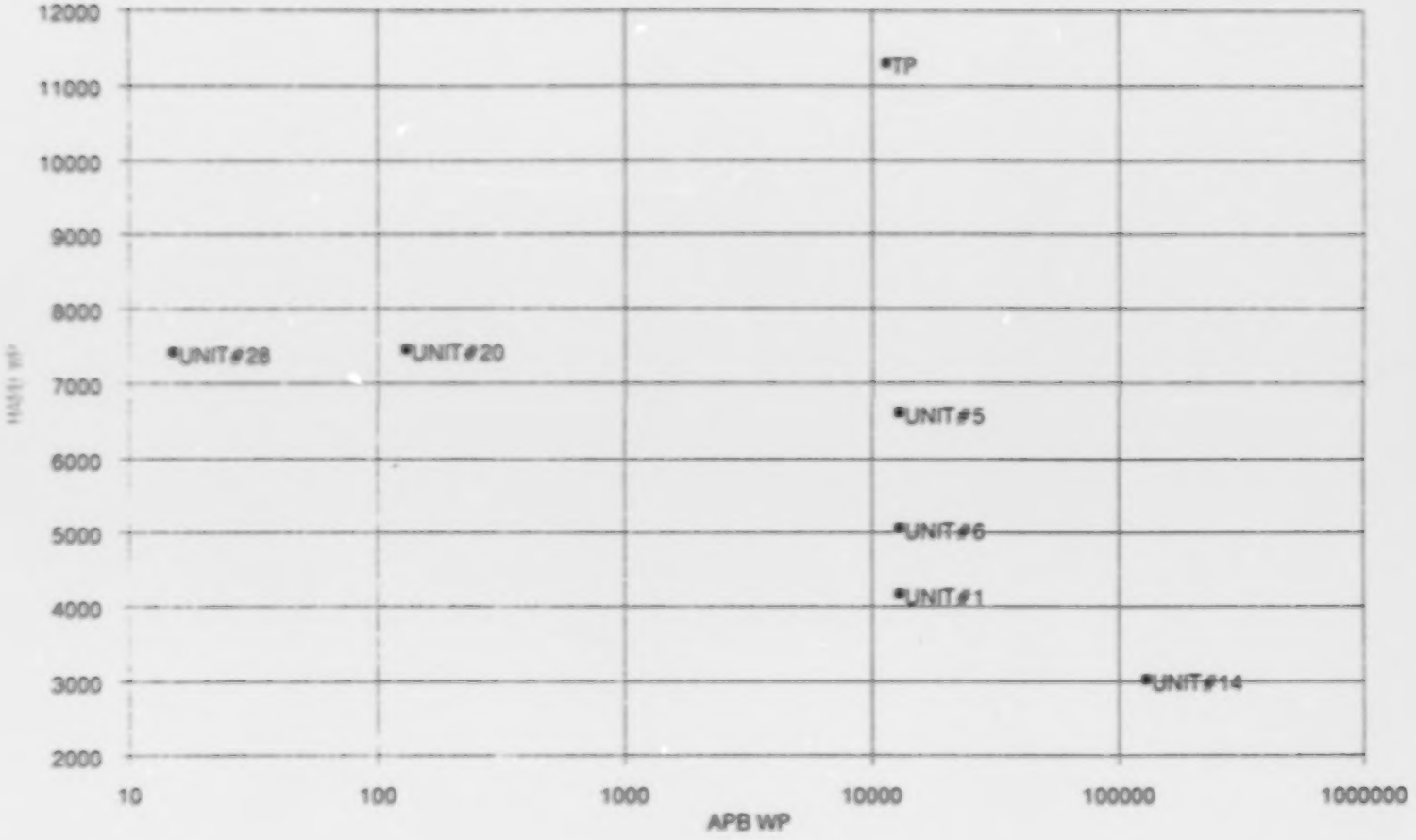

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Figure 24: Correlation of water hardness with density of sulfate reducing bacteria (SRB) in waterplant biofilms

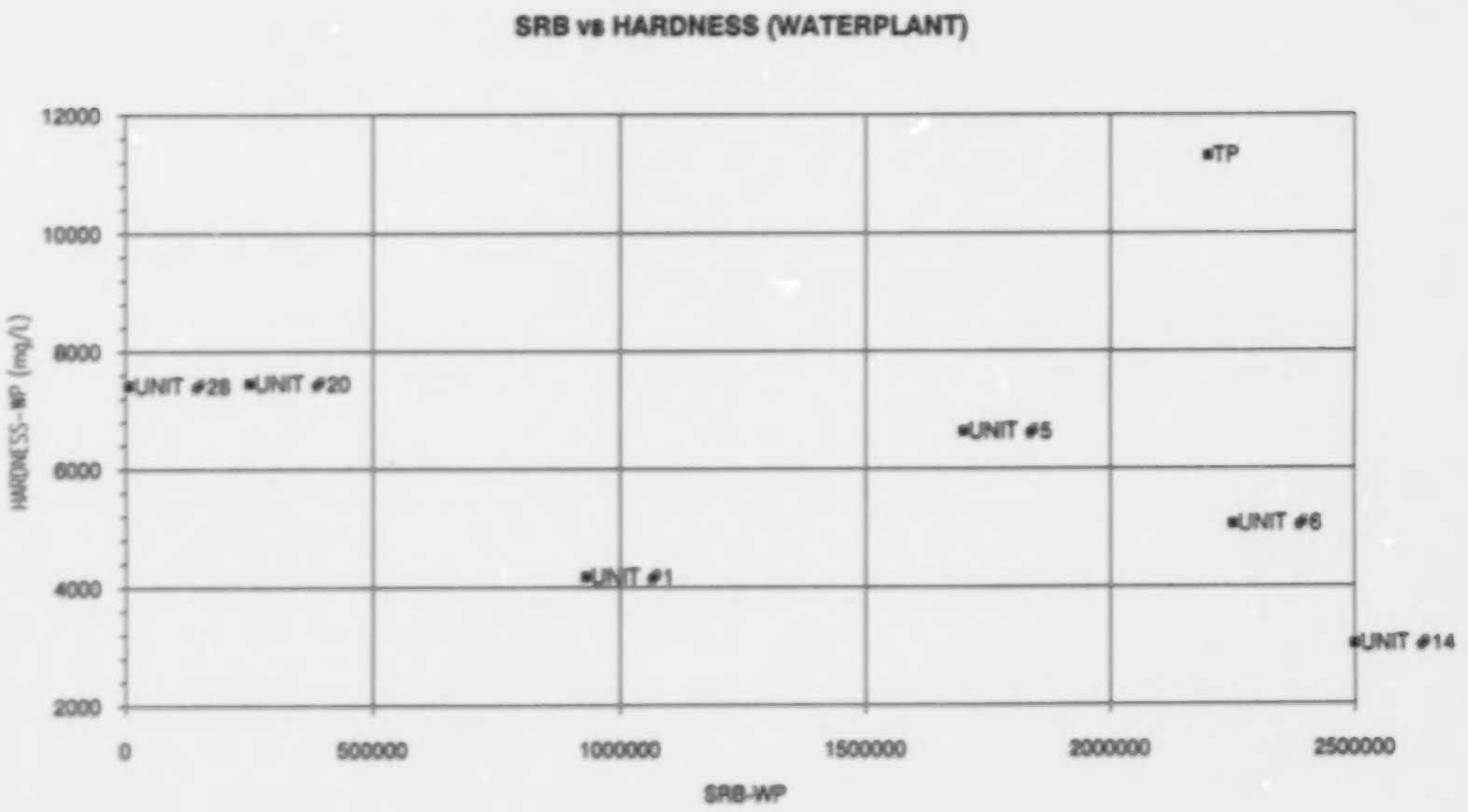

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Figure 25: Correlation of pH and density of acid producing bacteria (APB) in waterplant biofilms

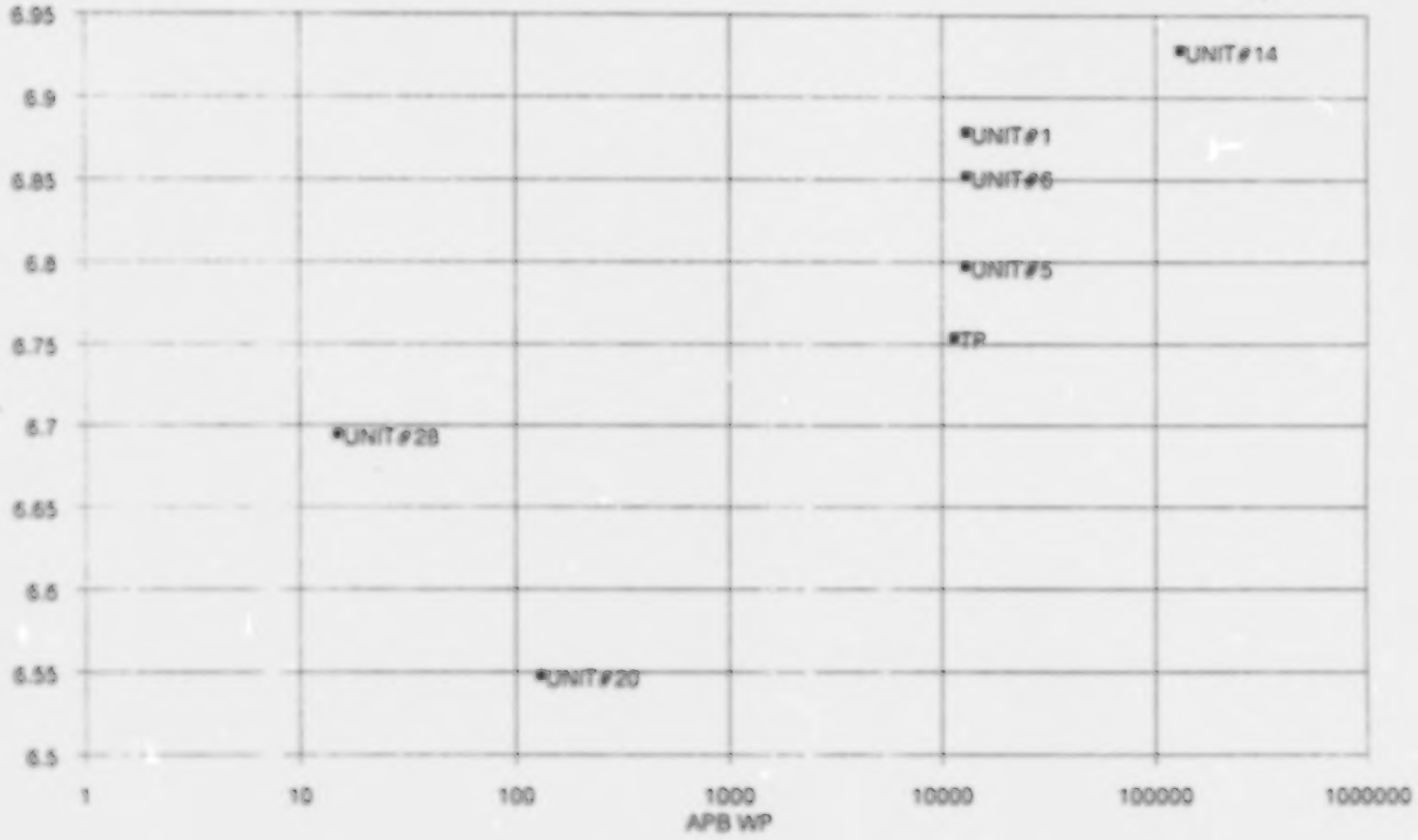

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Figure 26: Correlation of pH and density of sulfate reducing bacteria (SRB) in waterplant biofilms

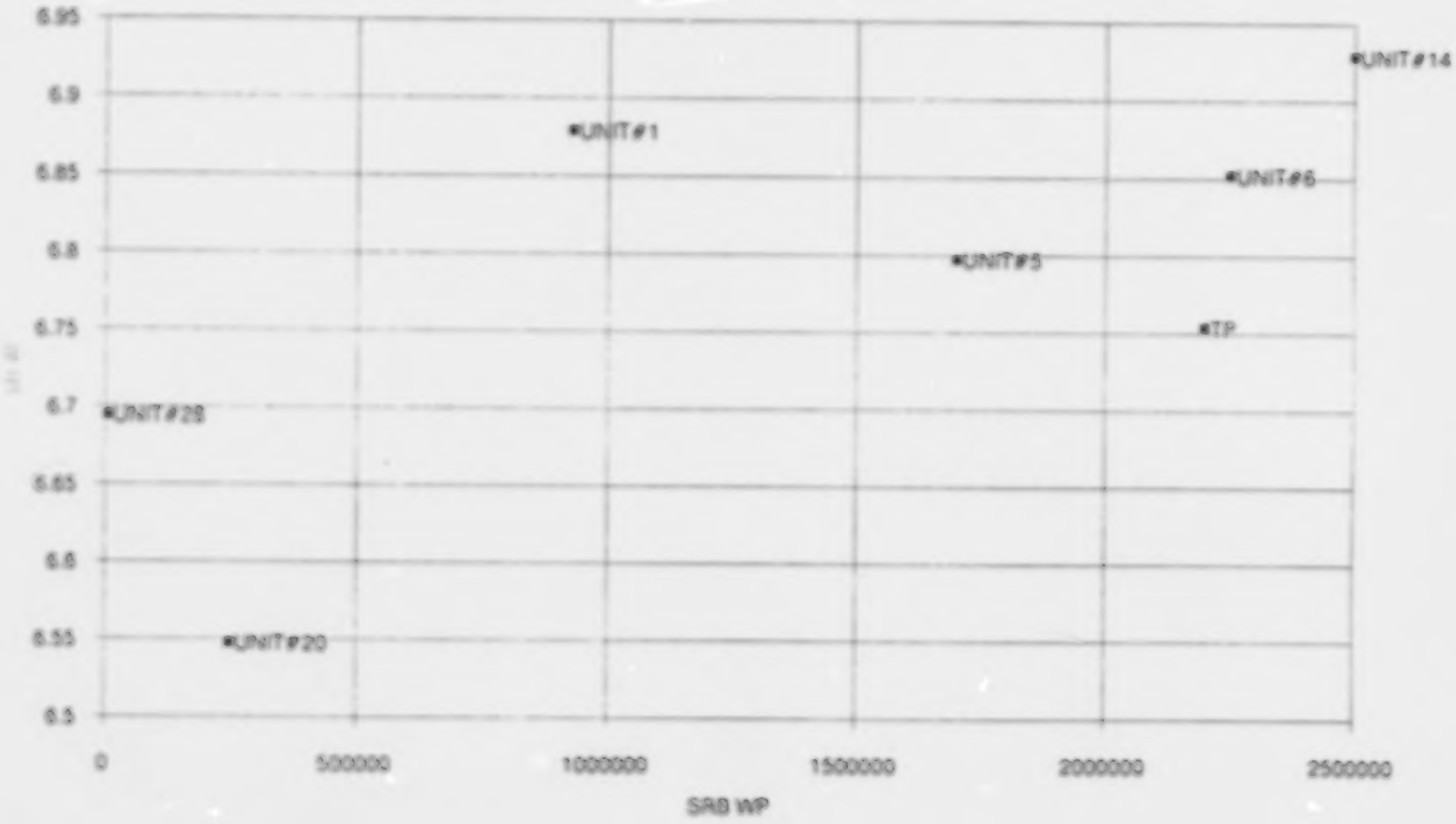

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Figure 27: Correlation of suspended solids and density of acid producing bacteria in free water knock out biofilms

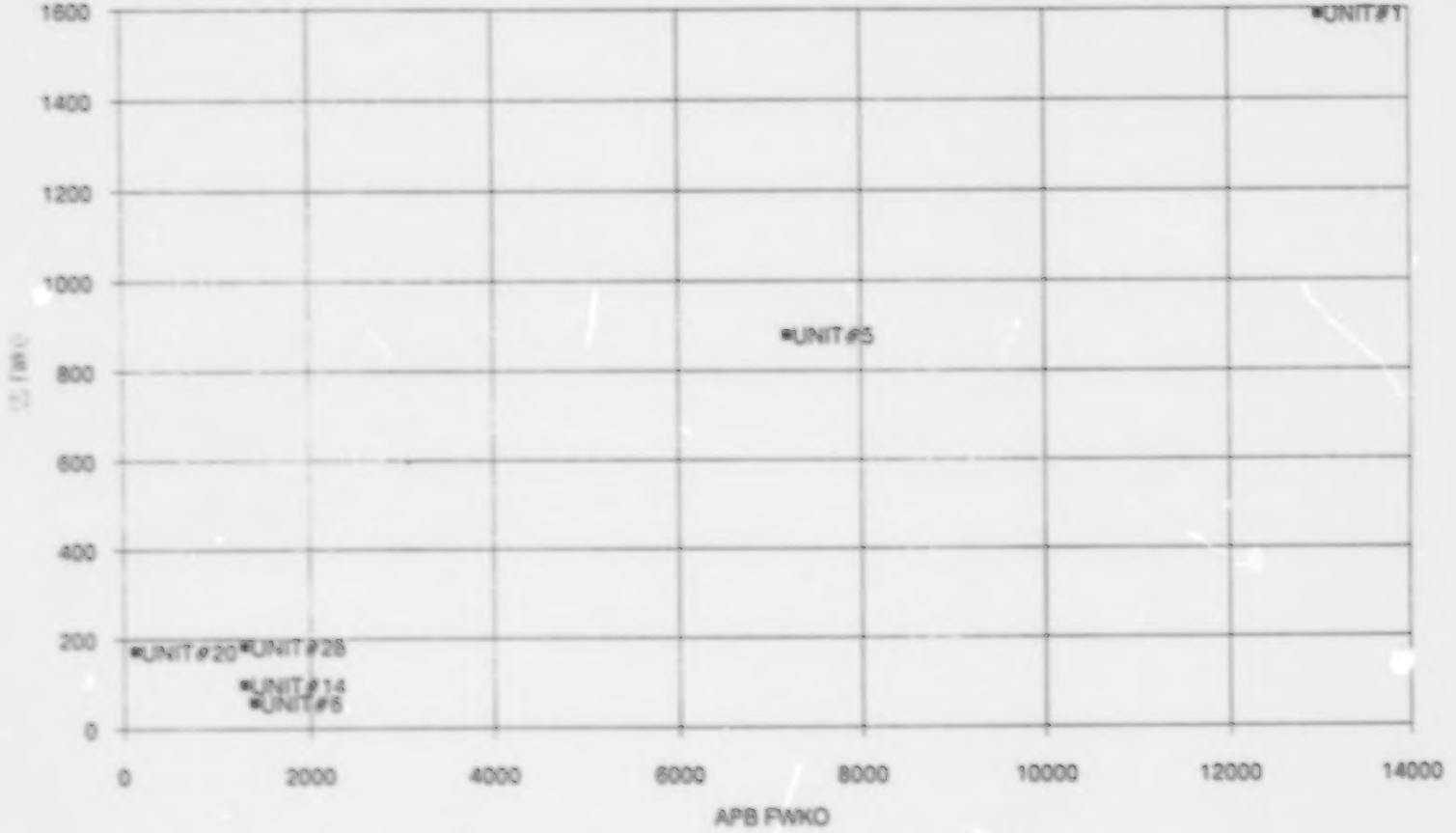

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Figure 28: Correlation of residual oxygen with density of acid producing bacteria (APB) in waterplant biofilms

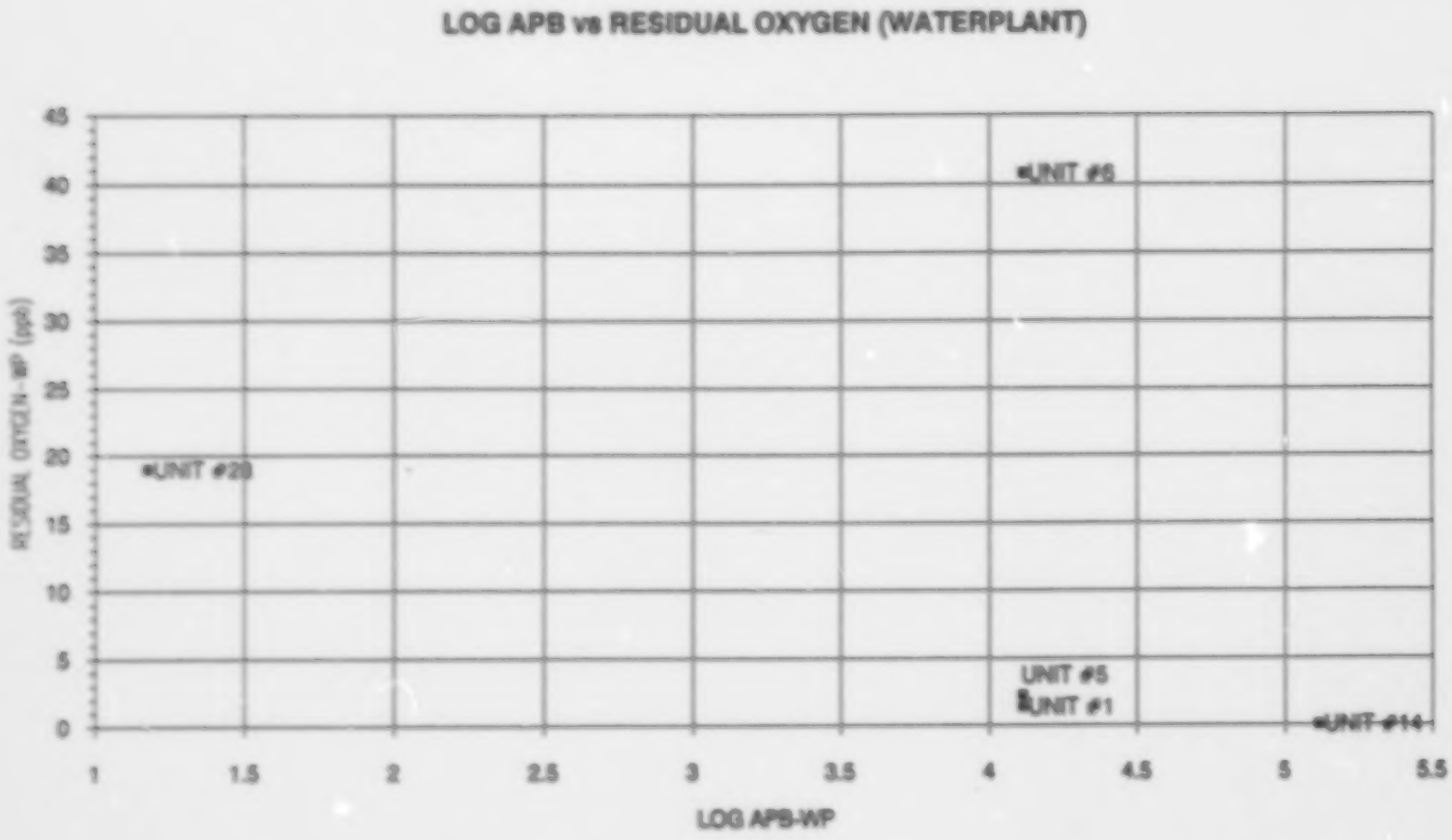

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Figure 29: Correlation of residual oxygen with density of acid producing bacteria (APB) in free water knock out biofilms

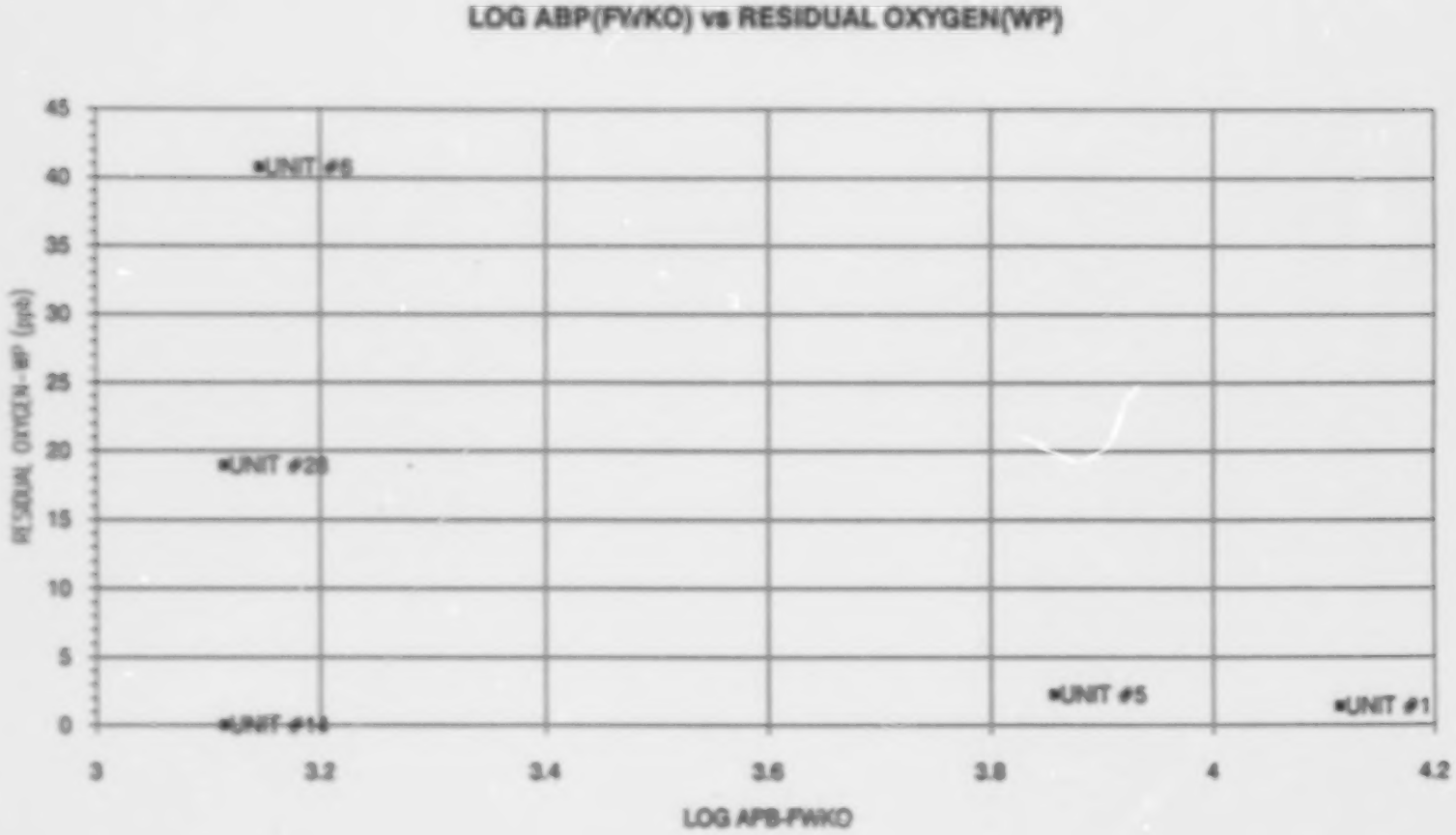

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Figure 29: Correlation of residual oxygen with density of acid producing bacteria (APB) in free water knock out biofilms

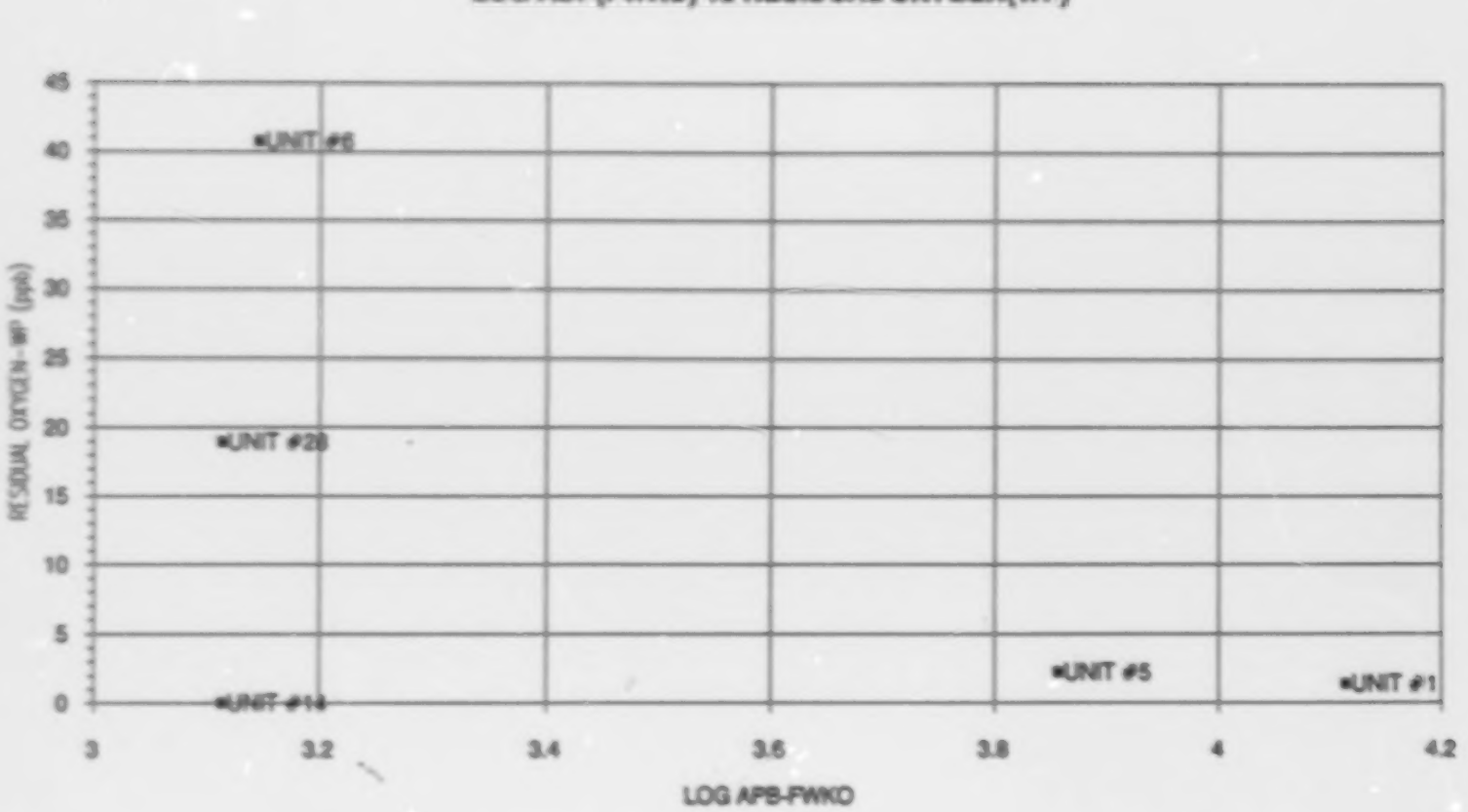

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Figure 30: Correlation of soluble sulfate with density of sulfate reducing bacteria in biofilms
(FWKO - Free Water Knock Out; WP - Waterplant)

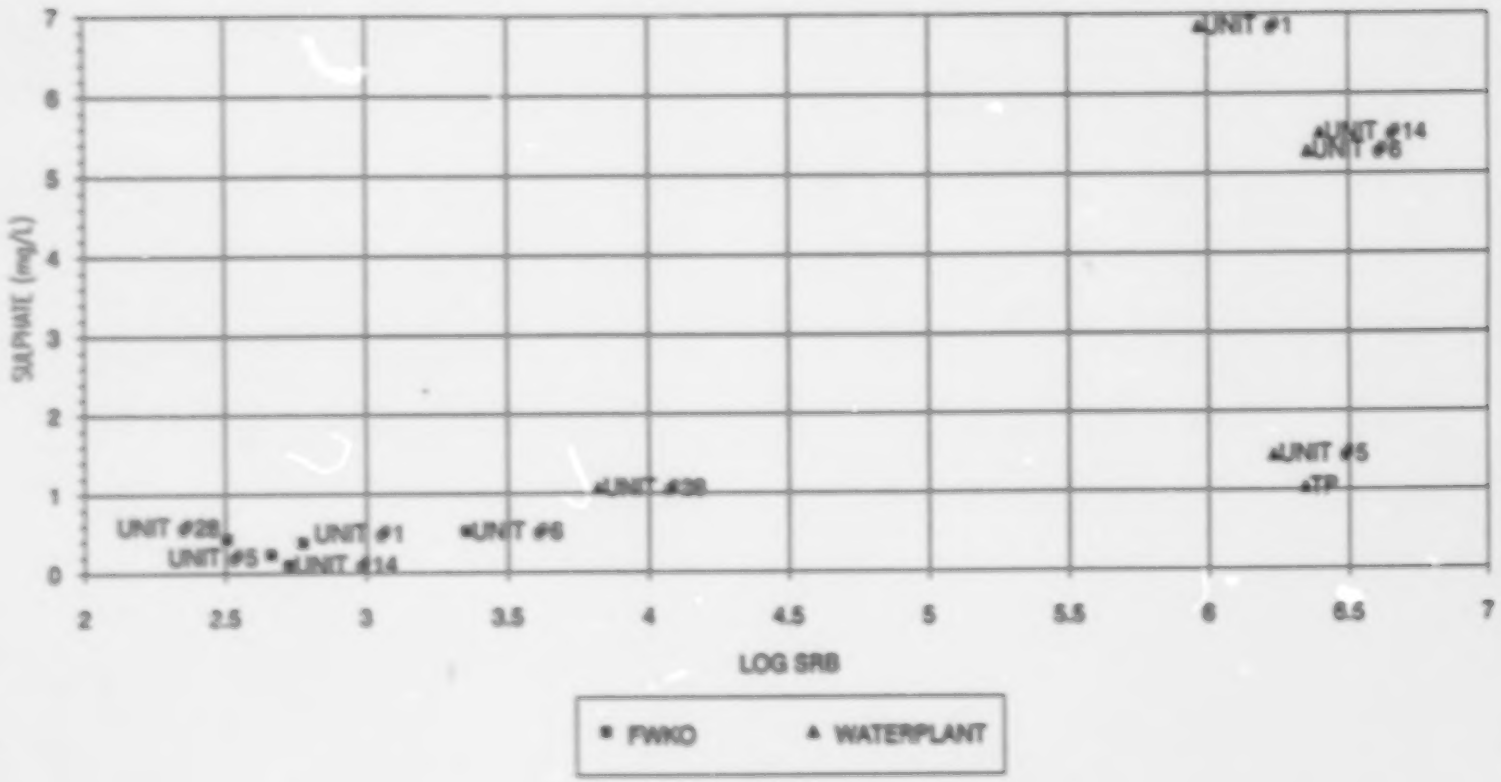

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Figure 31: Correlation of density of acid producing bacteria (APB) with residual sulfite in waterplants

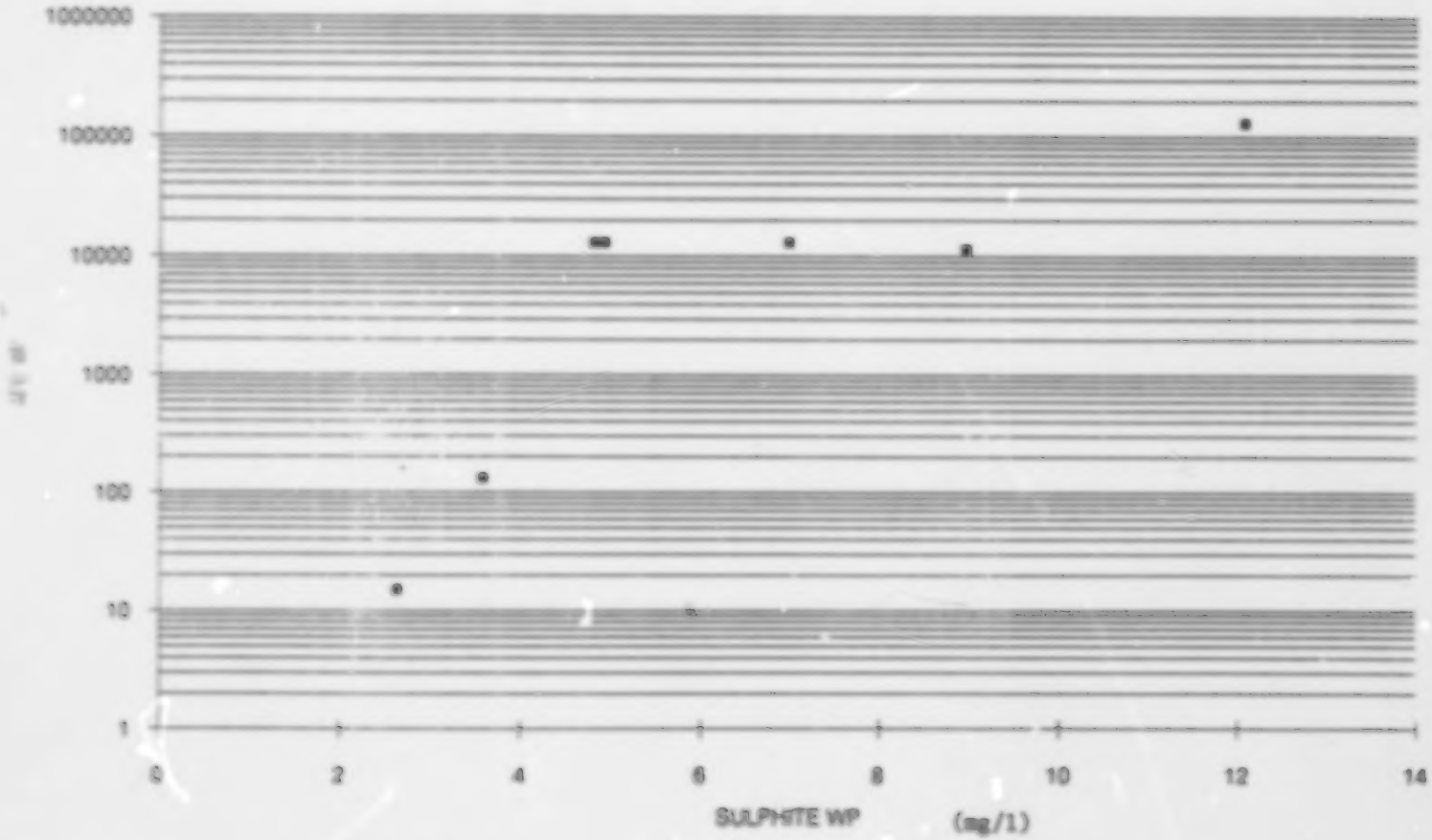

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Figure 32: Correlation of density of acid producing bacteria (APB) with residual scale inhibitor in waterplants

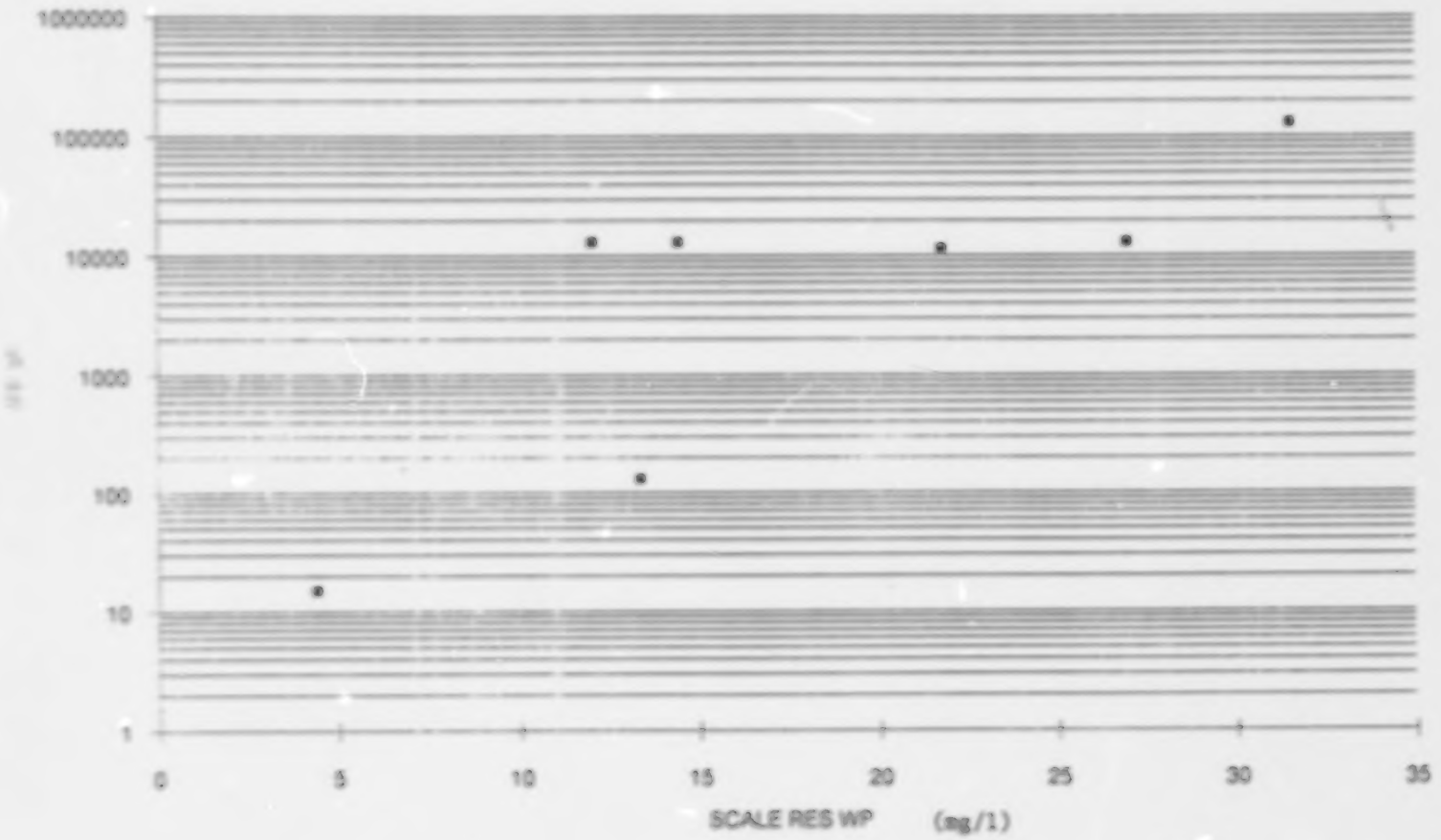

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Figure 33: Correlation of density of sulfate reducing bacteria (SRB) with residual sulfite in waterplants

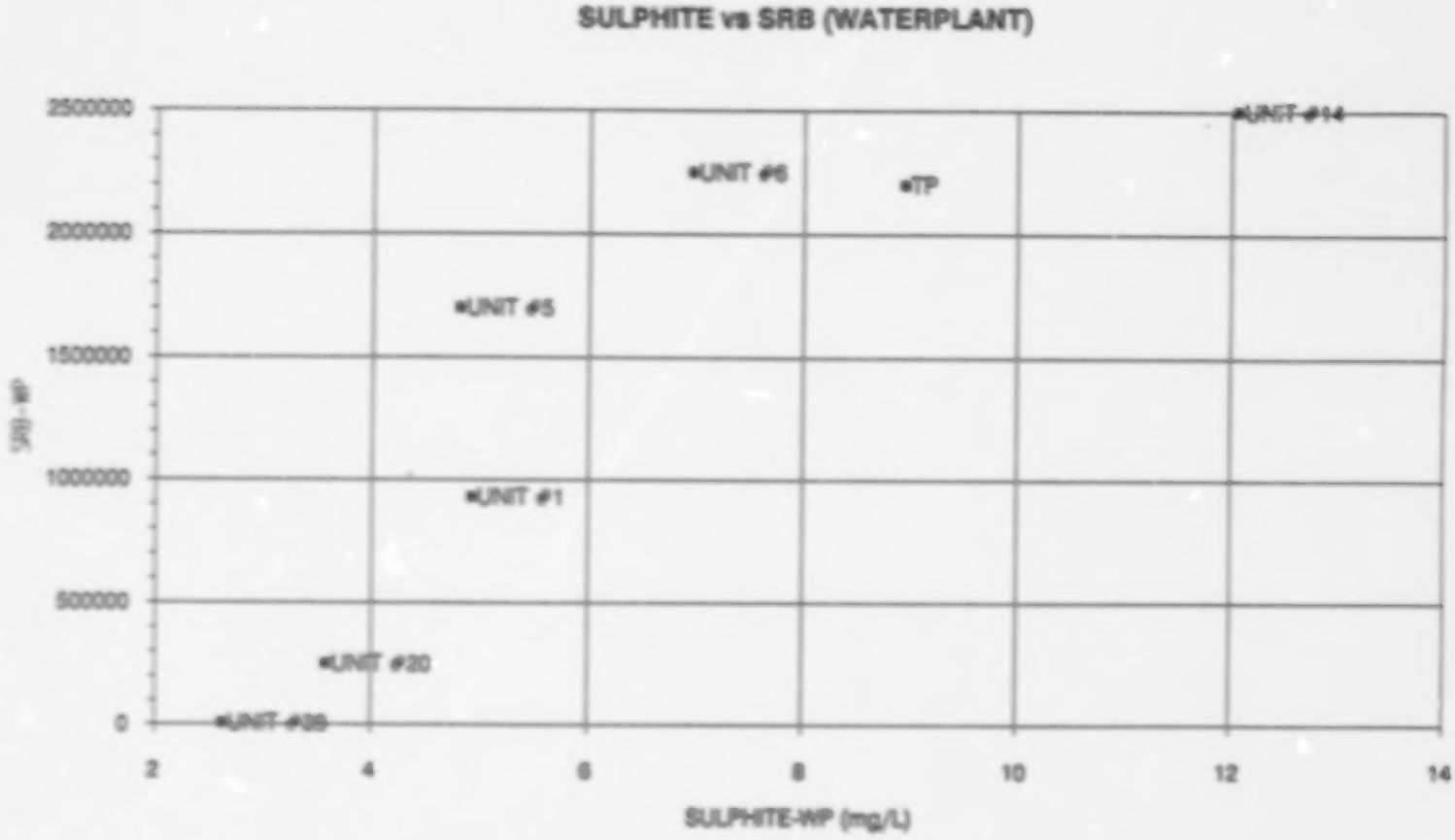

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Figure 34: Correlation of density of sulfate reducing bacteria (SRB) with residual scale inhibitor in waterplants

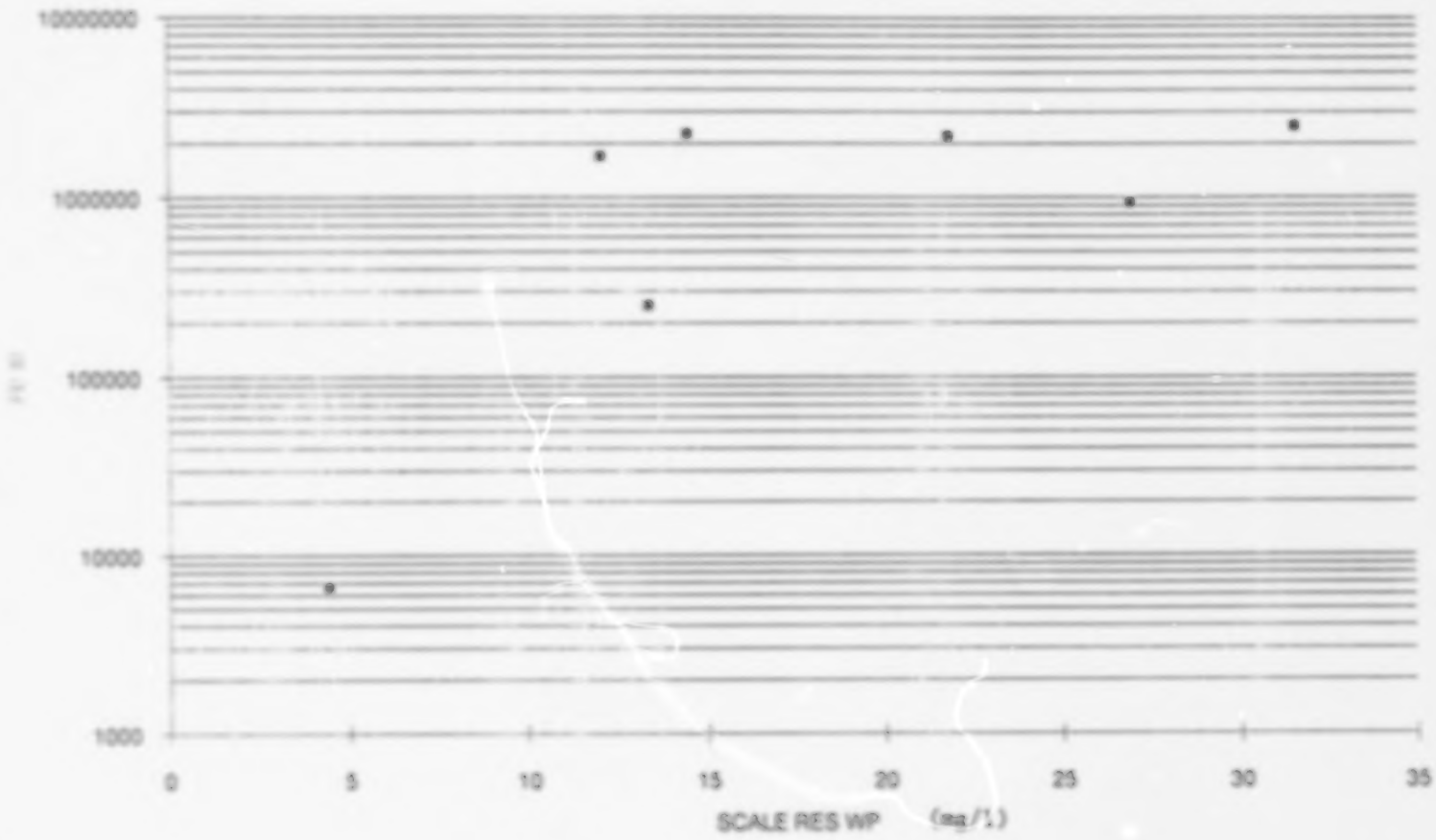

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Figure 25: Correlation of density of sulfate reducing bacteria (SRB) with residual corrosion inhibitor in free water knock outs

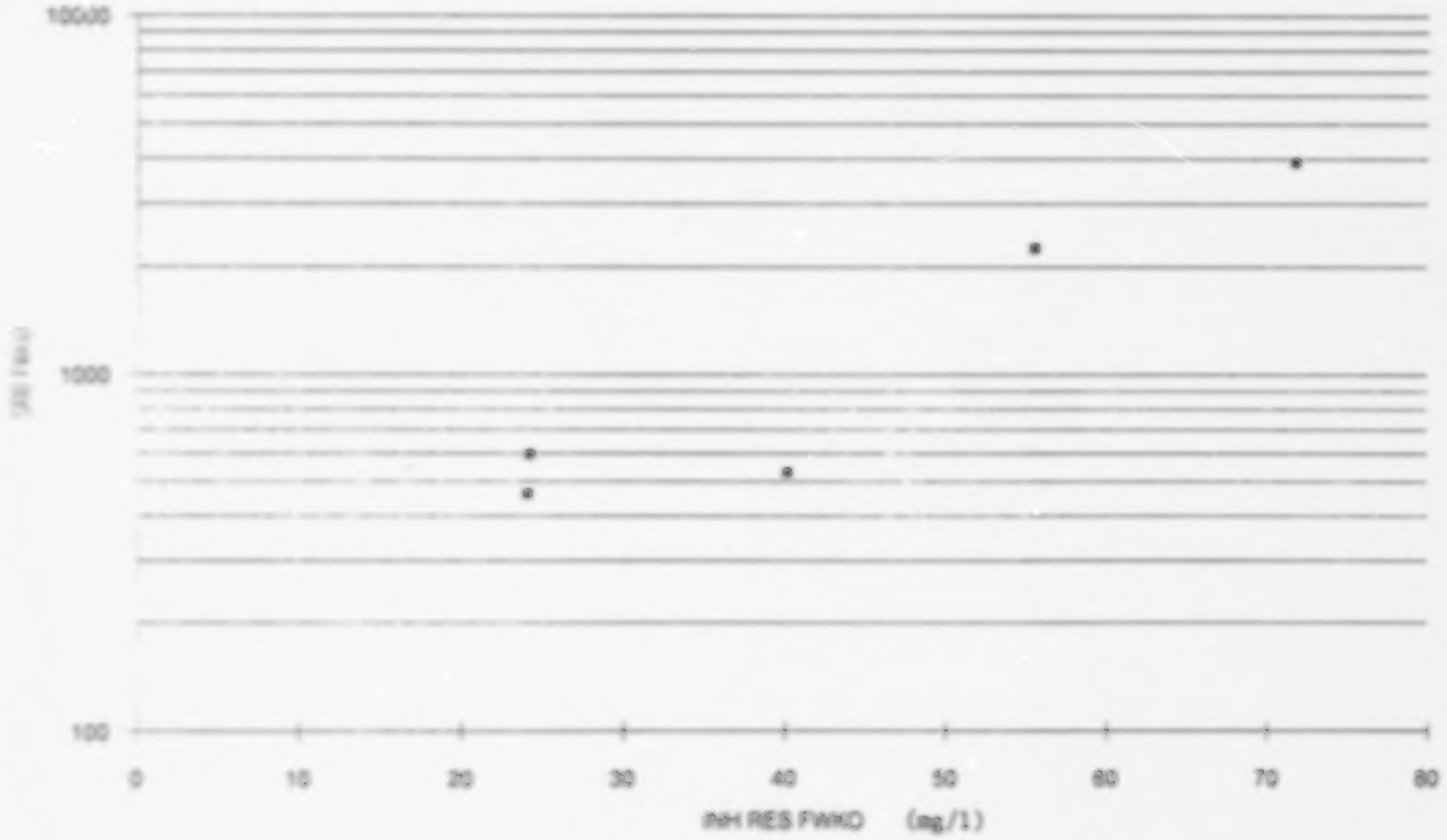

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Figure 36: Correlation of the increase in density of sulfate reducing bacteria (SRB) from free water knock out to waterplant with corrosion rates by weight loss coupon

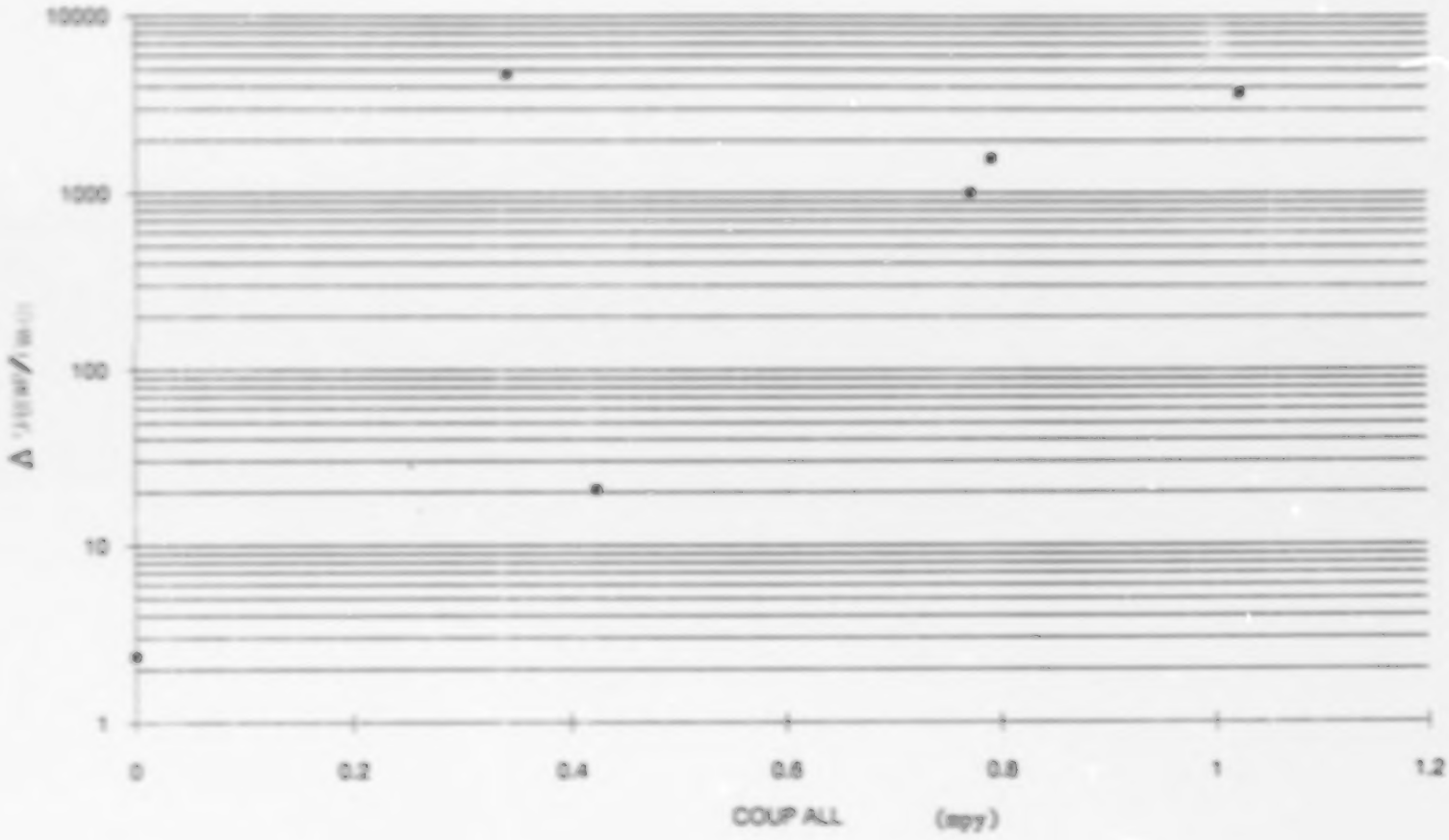

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Figure 37: Water analysis for nitrate in field test facility

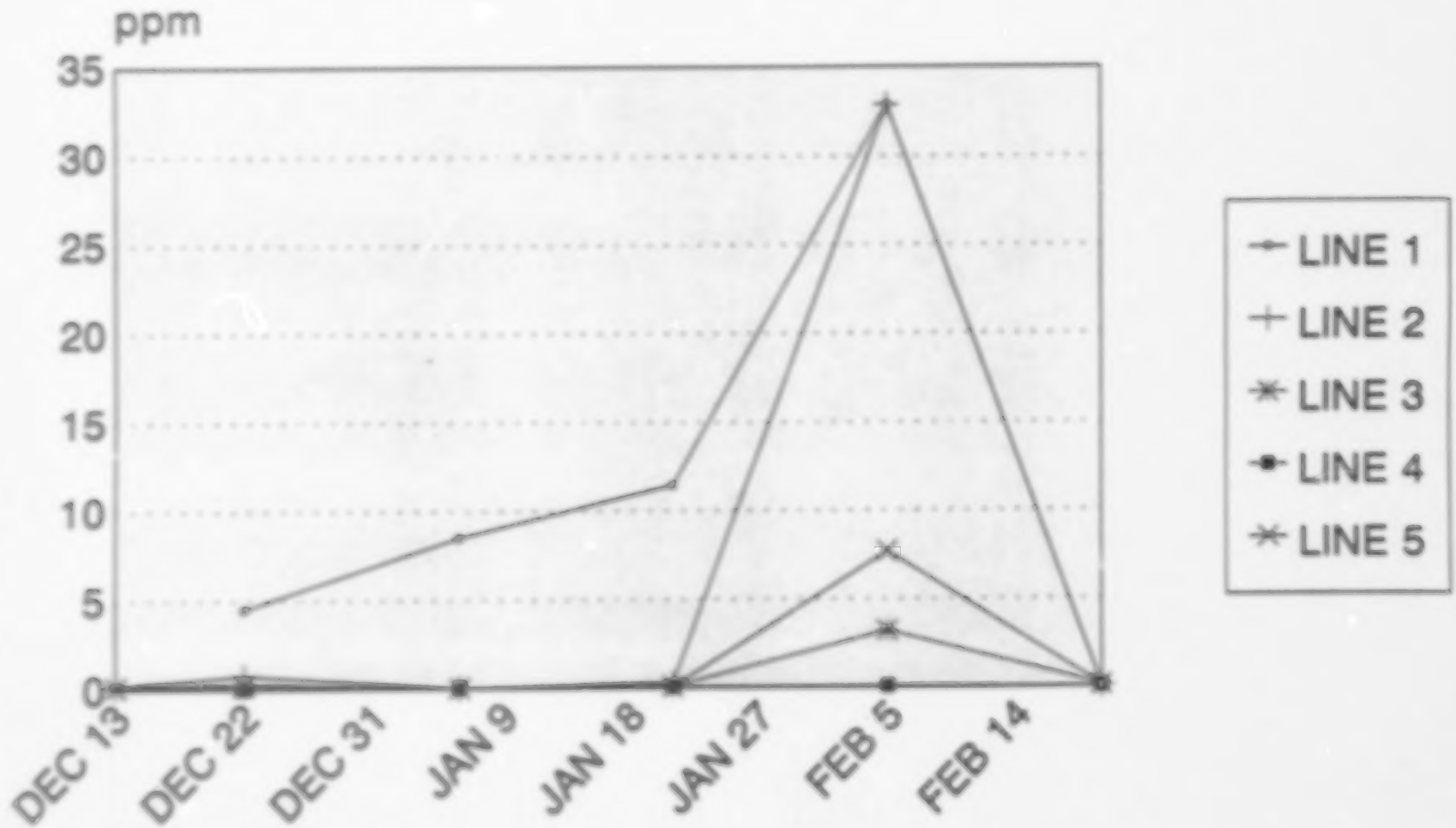

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Figure 39: Water analysis for residual sulfite from oxygen scavenger addition, line 5, field test facility

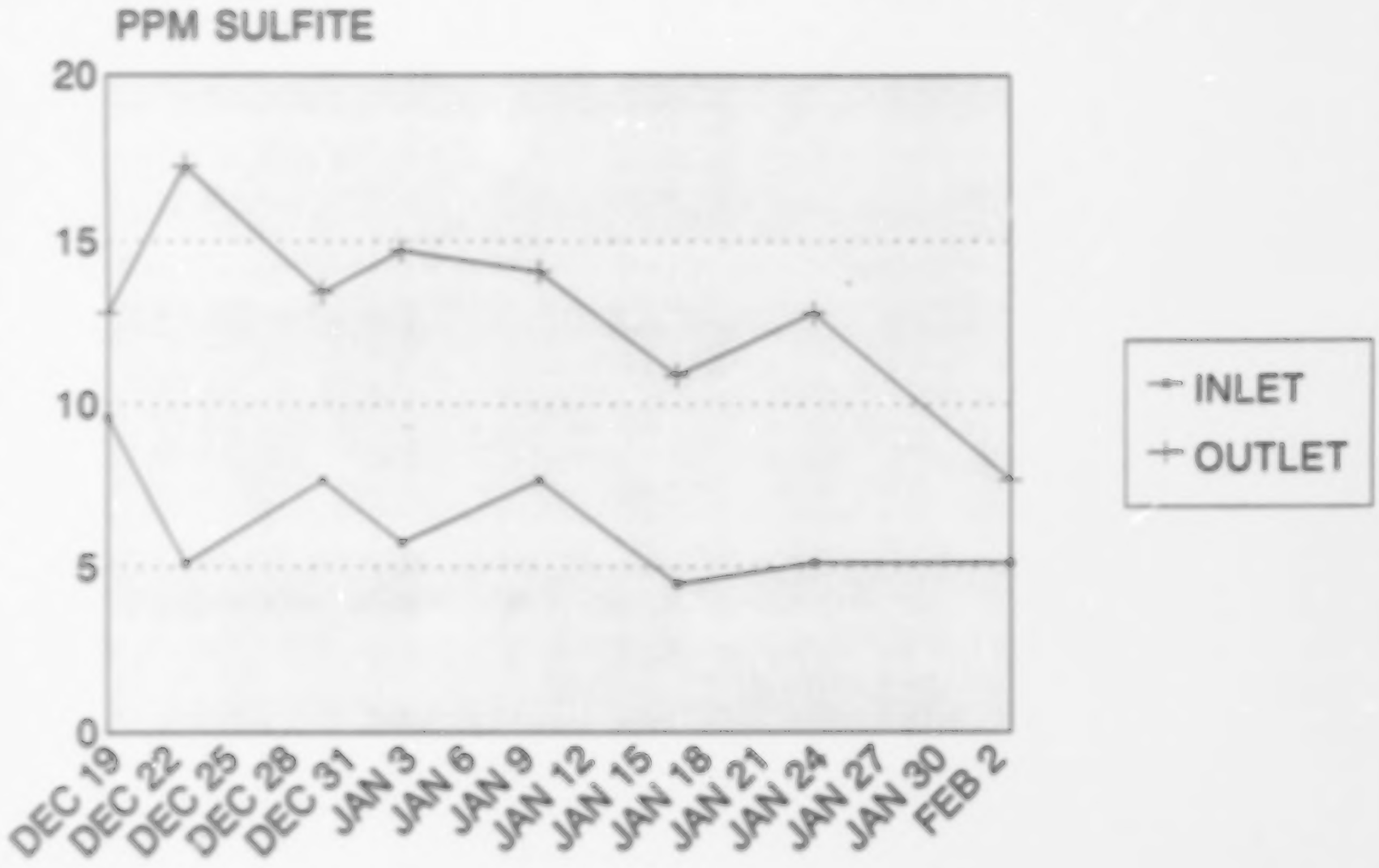

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Figure 39: Water analyses for sulfate in field test facility

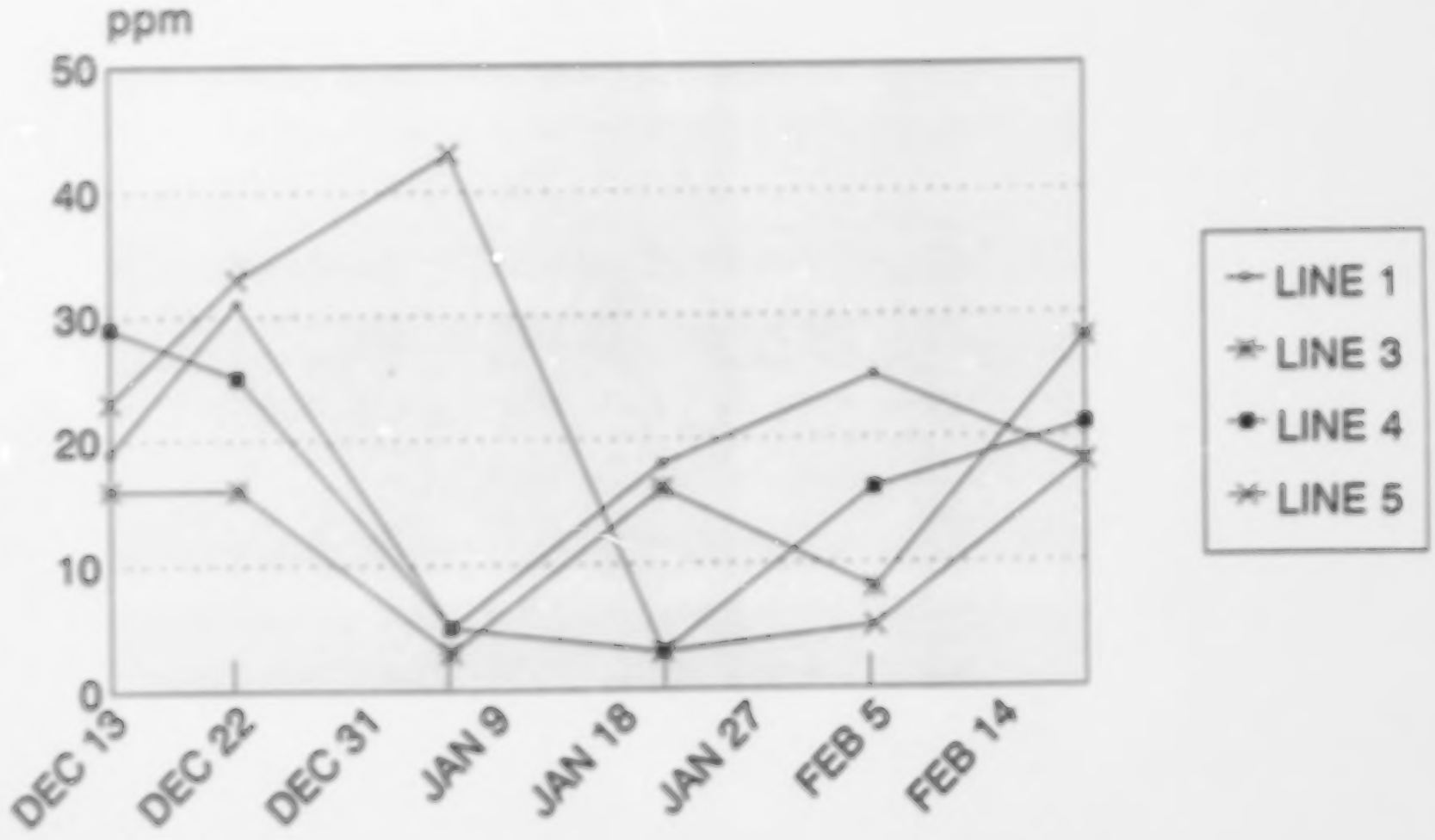

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Figure 40: Water analysis for sulfide in field test facility

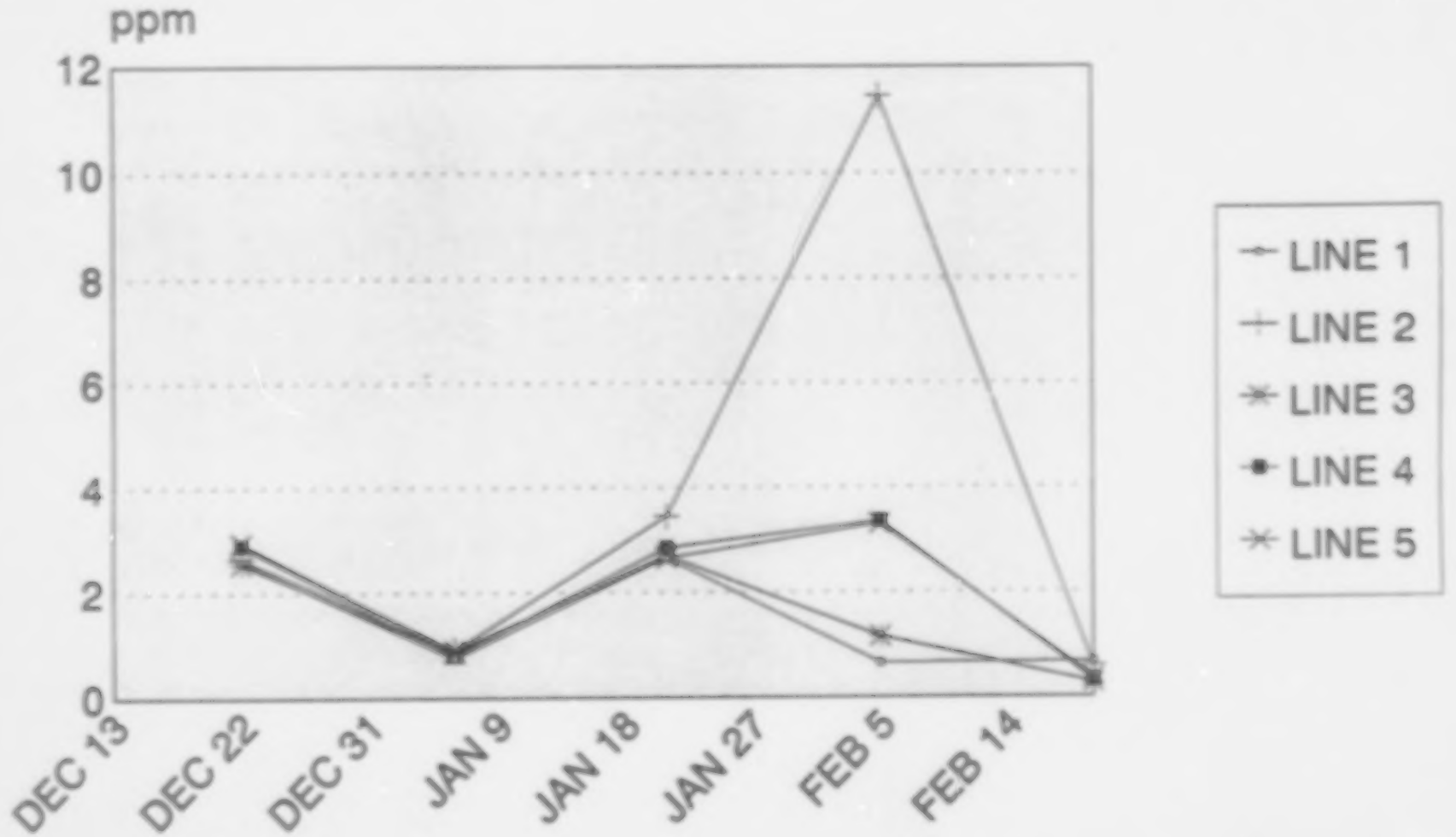

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Figure 41: Variation of microbial populations in line 1 + nitrate. (LAC-SRB = Lactate utilizing sulfate reducing bacteria; ACE-SRB = Acetate utilizing bacteria; APB = Acid producing bacteria)

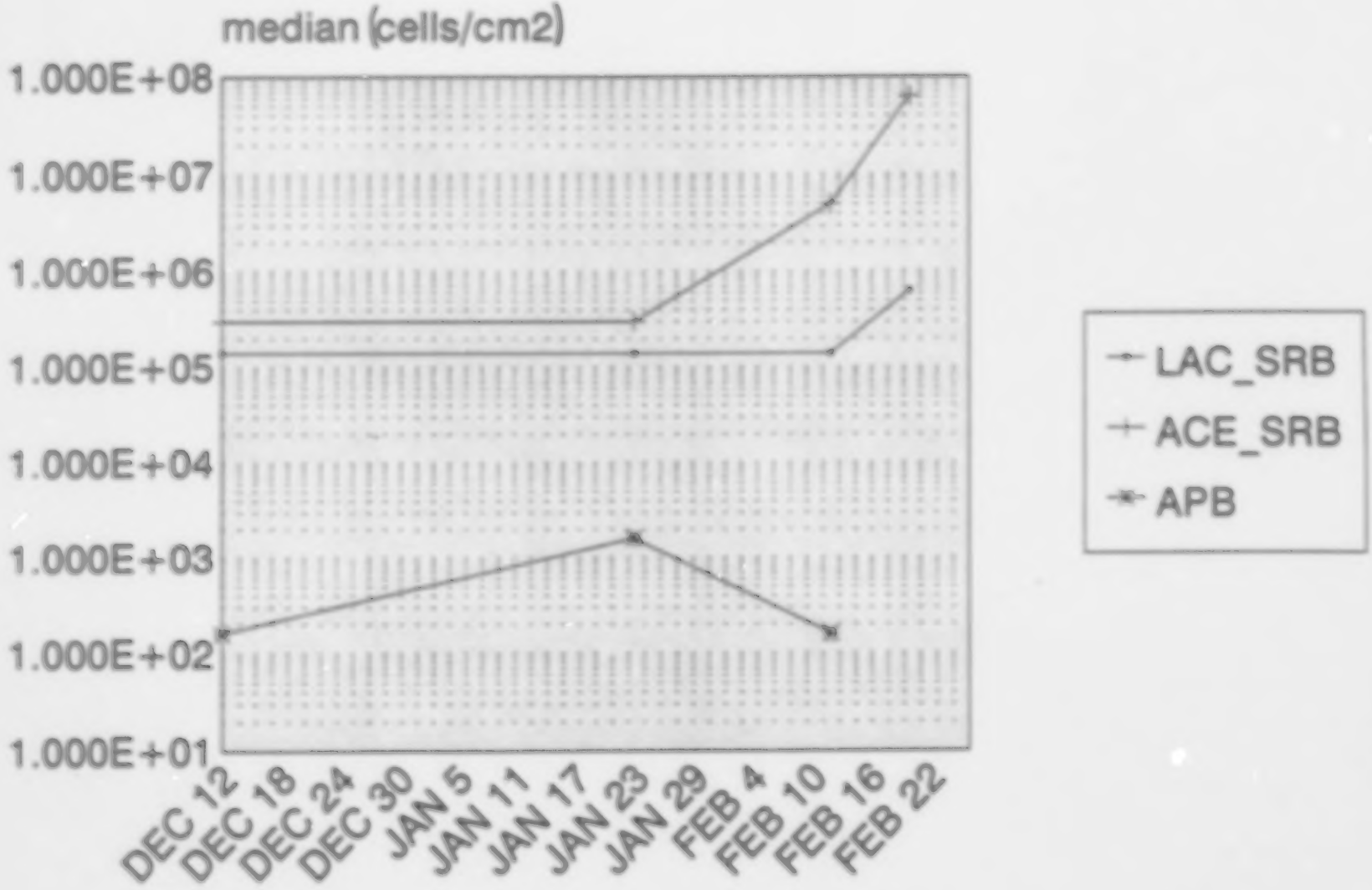

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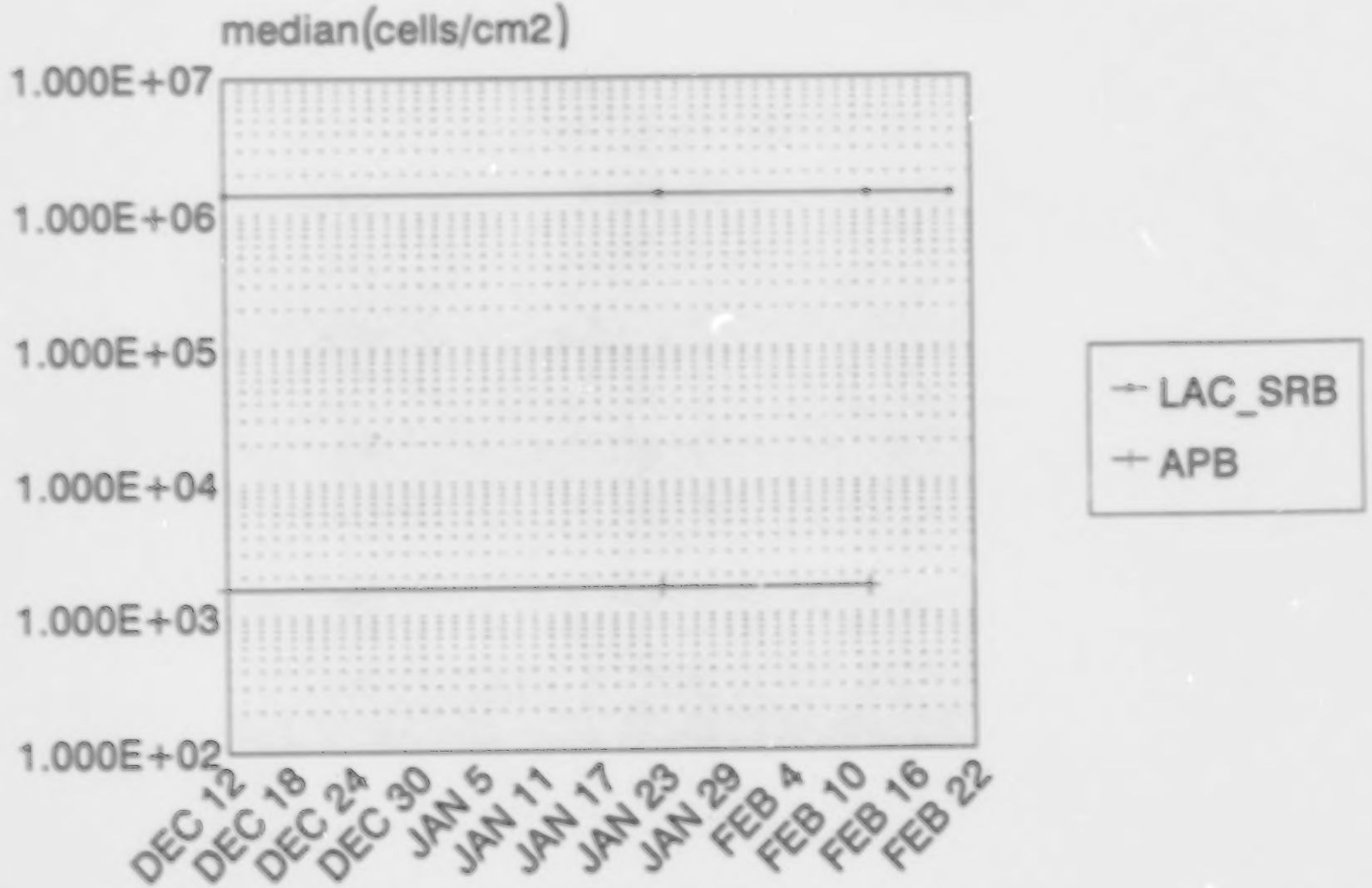
Figure 42: Variation of microbial populations in line 2 laminar flow. (LAC-SRB = Lactate utilizing sulfate reducing bacteria; APB = Acid producing bacteria



* LAMINAR FLOW COMMENCED DECEMBER 25, 1991

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Figure 43: Variation of microbial populations in line 3 control (LAC-SRB = Lactate utilizing sulfate reducing bacteria; ACE-SRB = Acetate utilizing bacteria; APB = Acid producing bacteria)

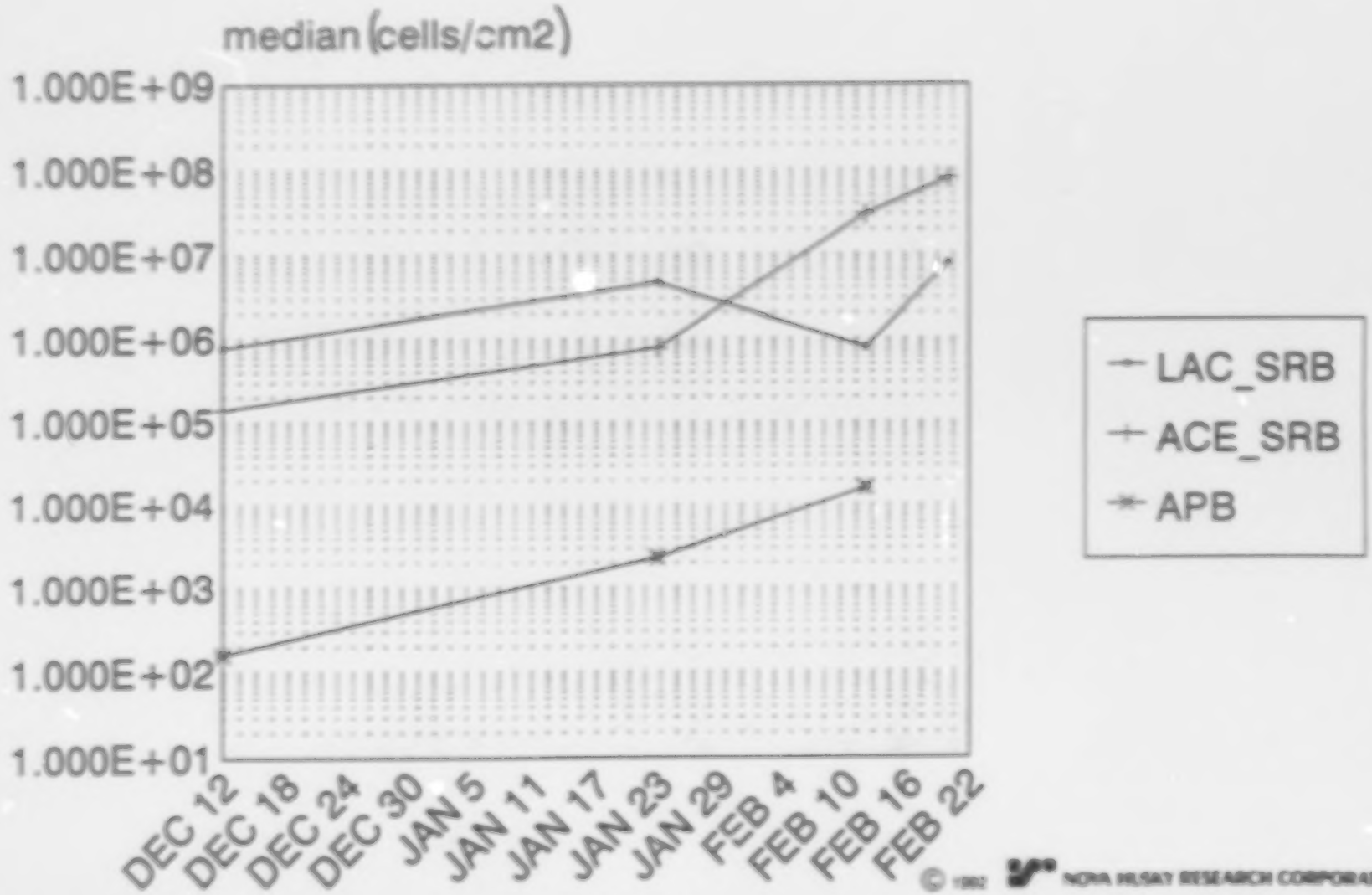

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Figure 44: Variation of microbial populations in line 4 - acetate/lactate (LAC-SRB = Lactate utilizing sulfate reducing bacteria; ACE-SRB = Acetate utilizing bacteria; APB = Acid producing bacteria)

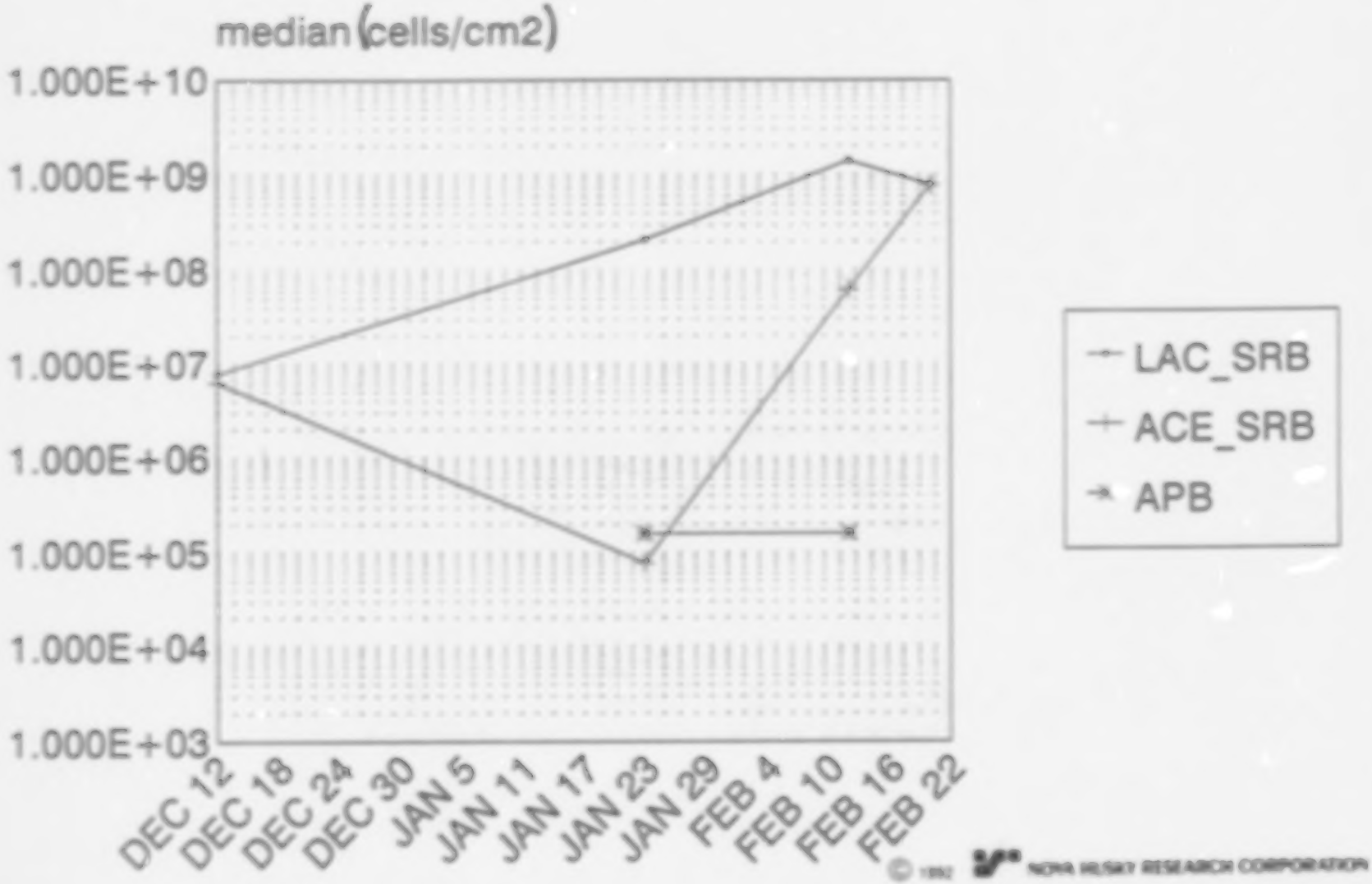

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Figure 45: Variation of microbial populations in line 5 + oxygen scavenger (LAC-SRB = Lactate utilizing sulfate reducing bacteria; ACE-SRB = Acetate utilizing bacteria; APB = Acid producing bacteria)

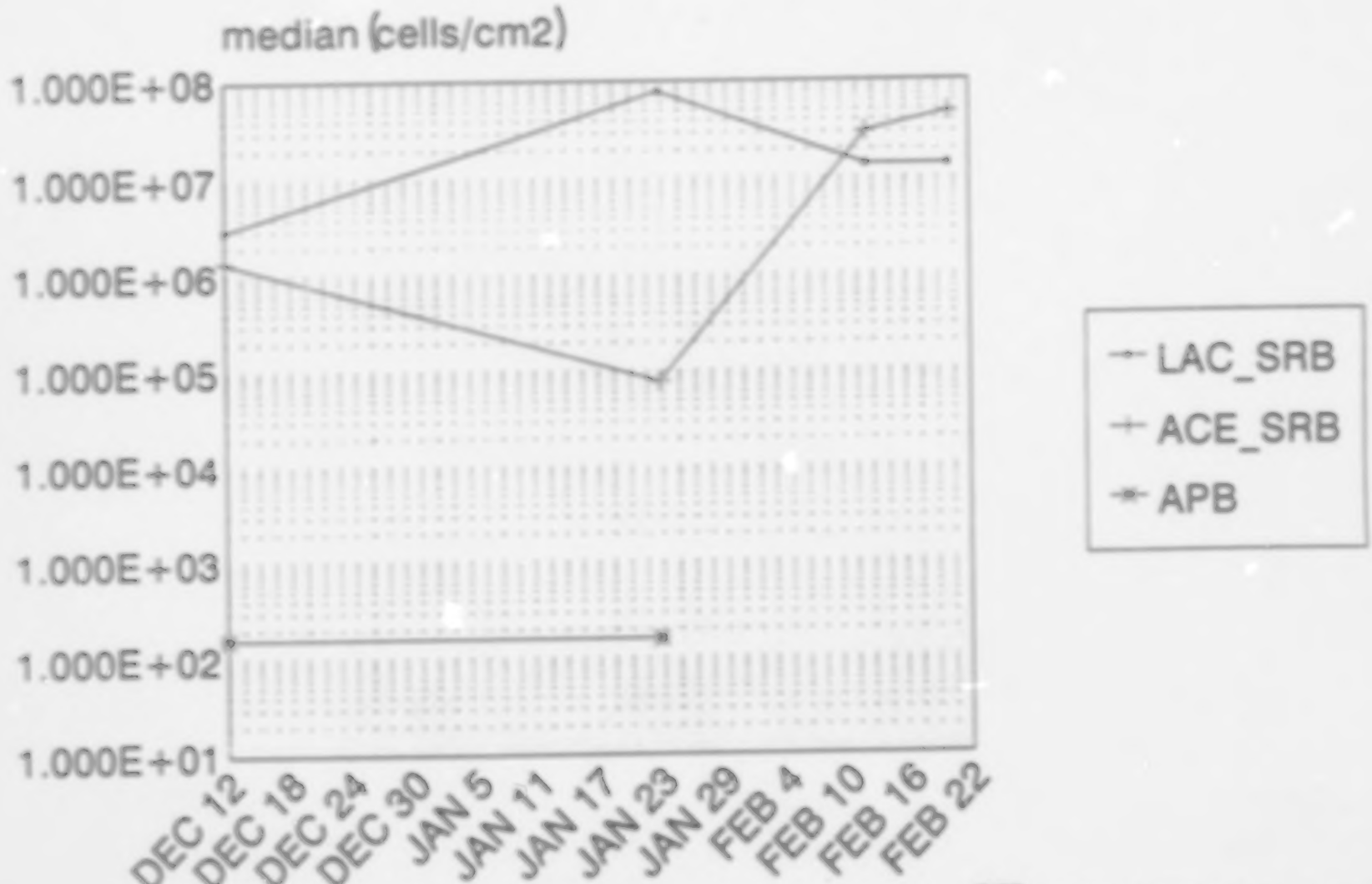

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Figure 46: Comparison of changes in population densities for lactate utilizing sulfate reducing bacteria in all lines, field test facility

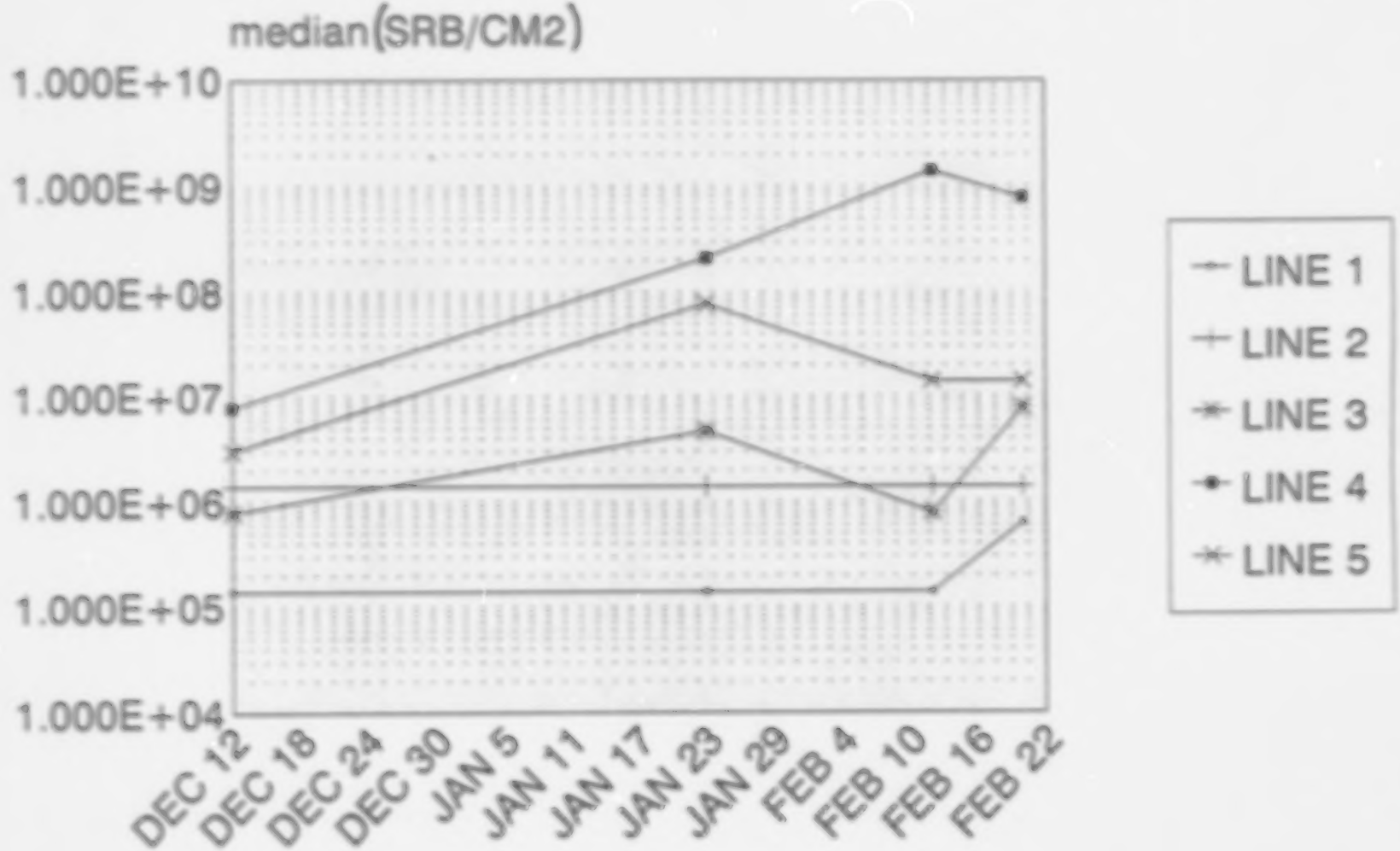

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Figure 47: Comparison of changes in population densities for acetate utilizing sulfate reducing bacteria in all lines, field test facility

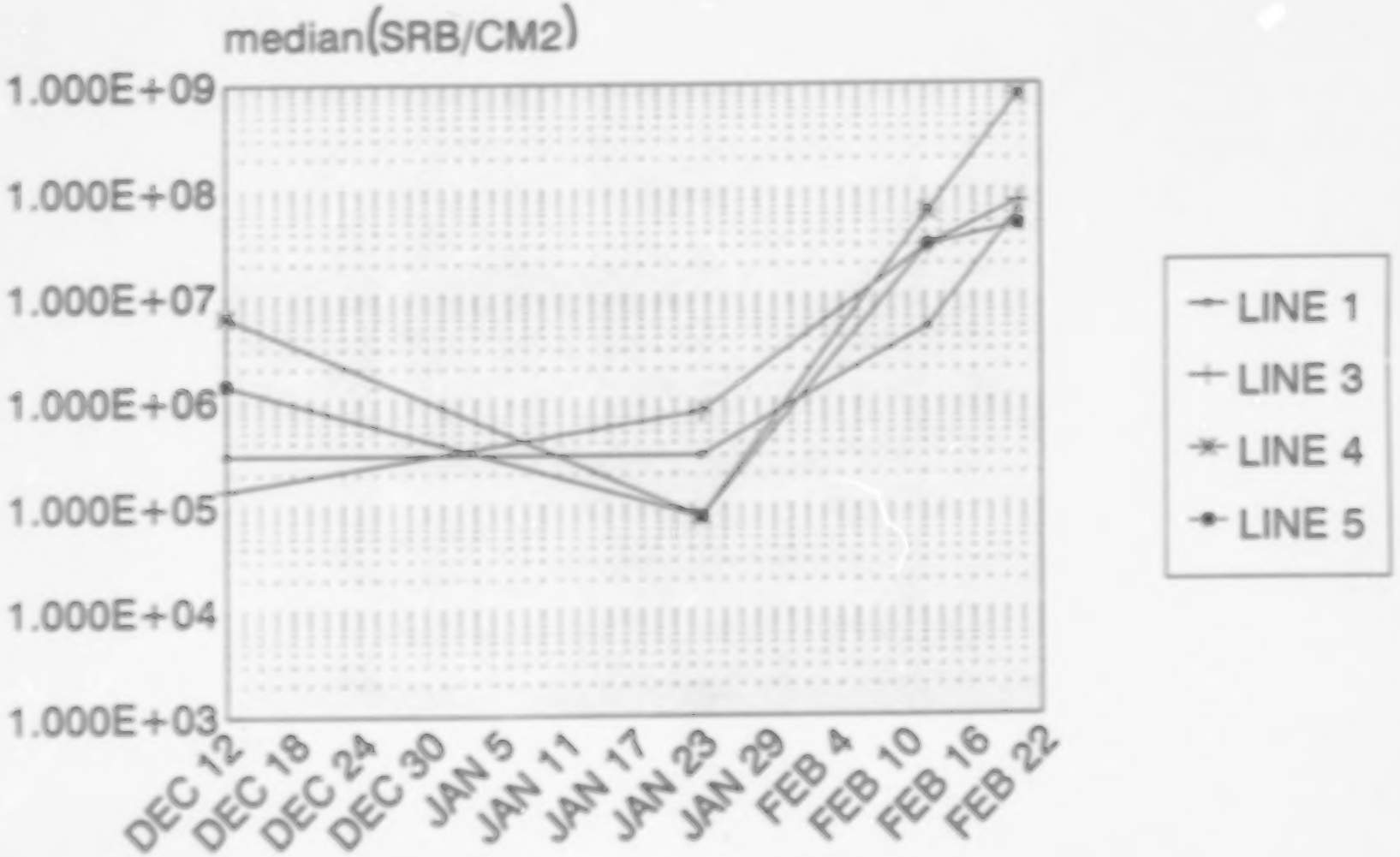

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Figure 48: Variation of lactate utilizing sulfate reducing bacteria (average viable cells/cm^2) and sulfate reducing capacity, line 1 + nitrate

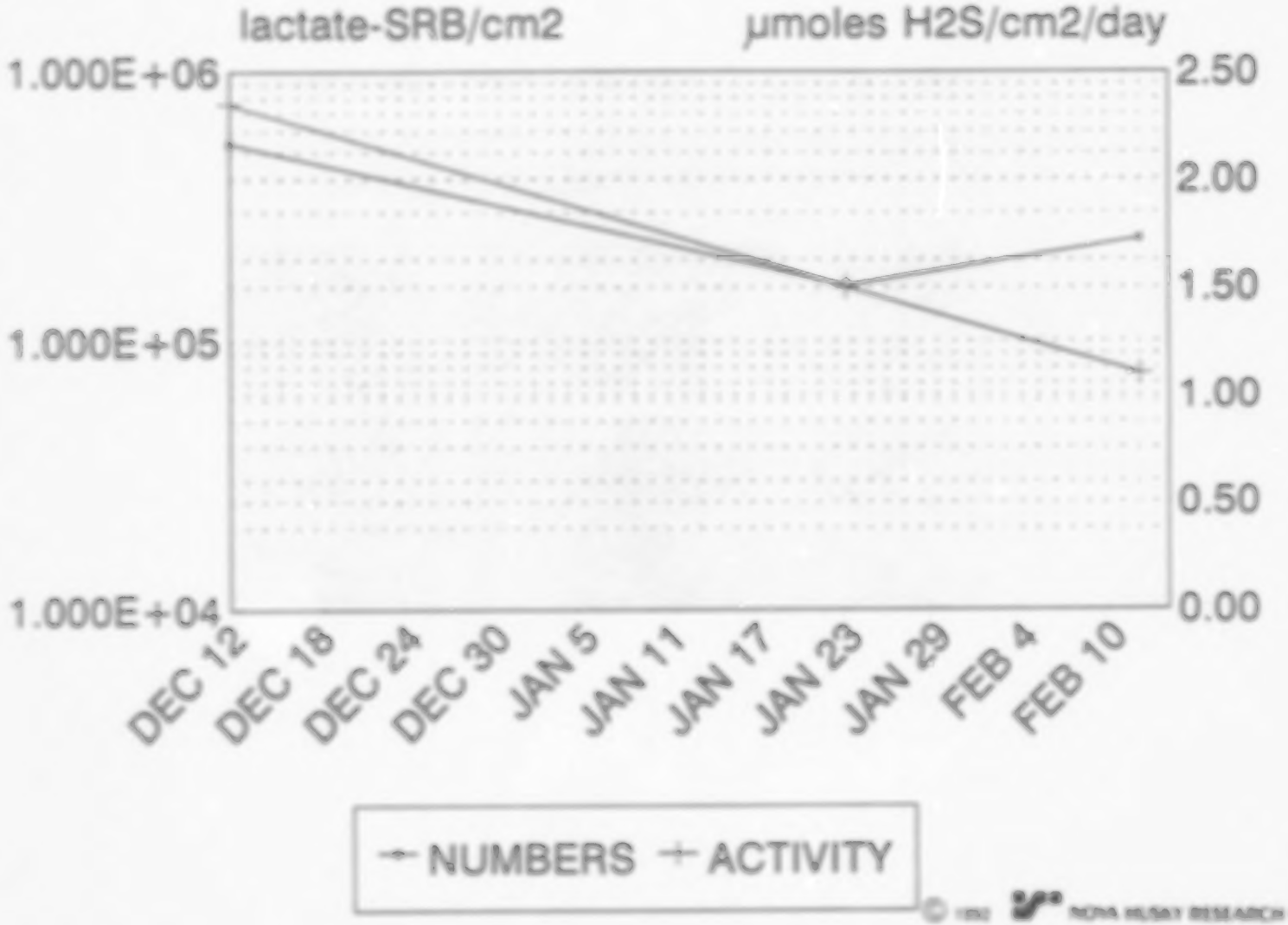

Figure 49: Variation of lactate utilizing sulfate reducing bacteria (average viable cells/cm^2) and sulfate reducing capacity, line 2, laminar flow

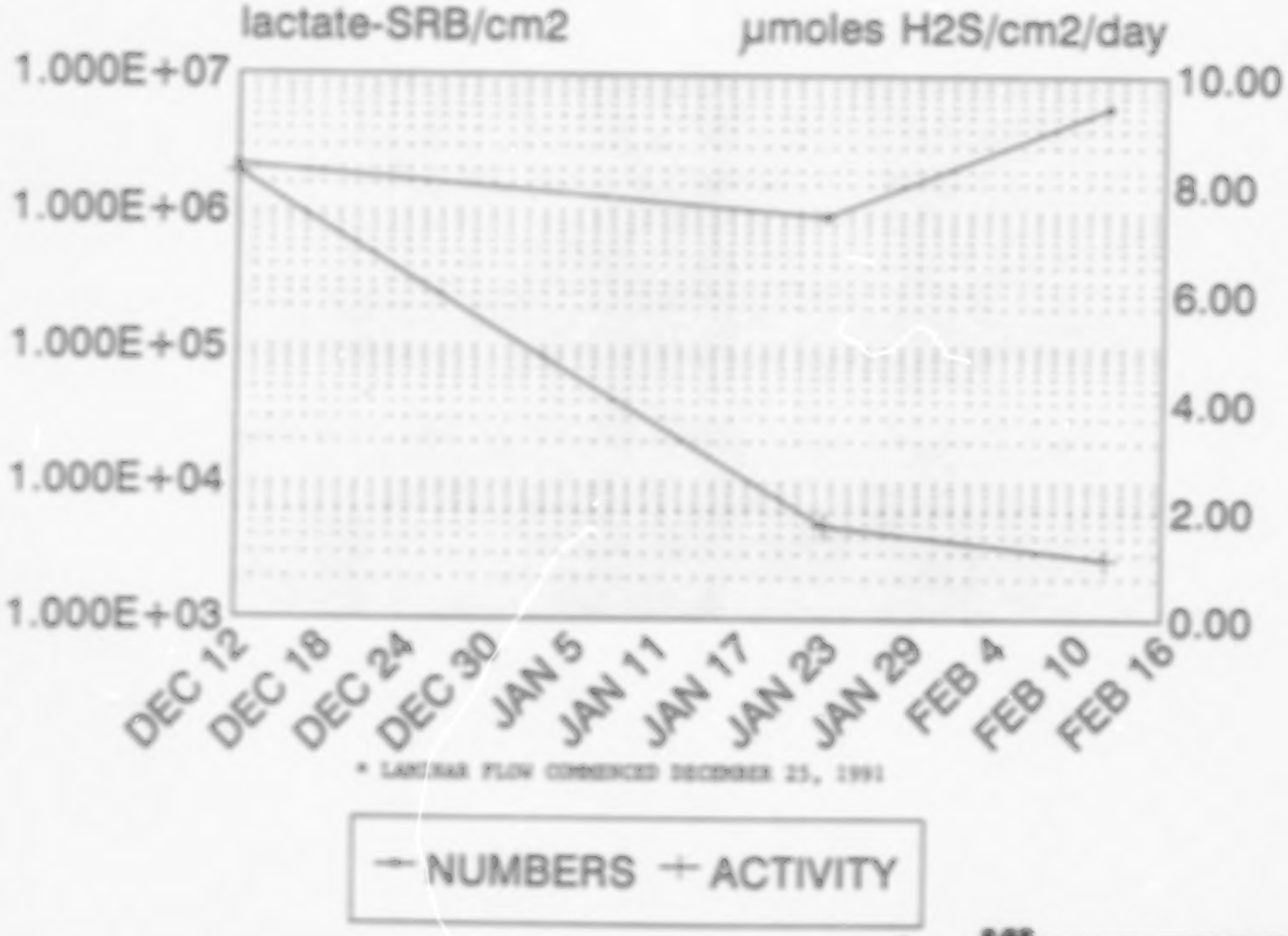

Figure 50: Variation of lactate utilizing sulfate reducing bacteria and sulfate reducing capacity (average viable cells/cm^2) line 3, control

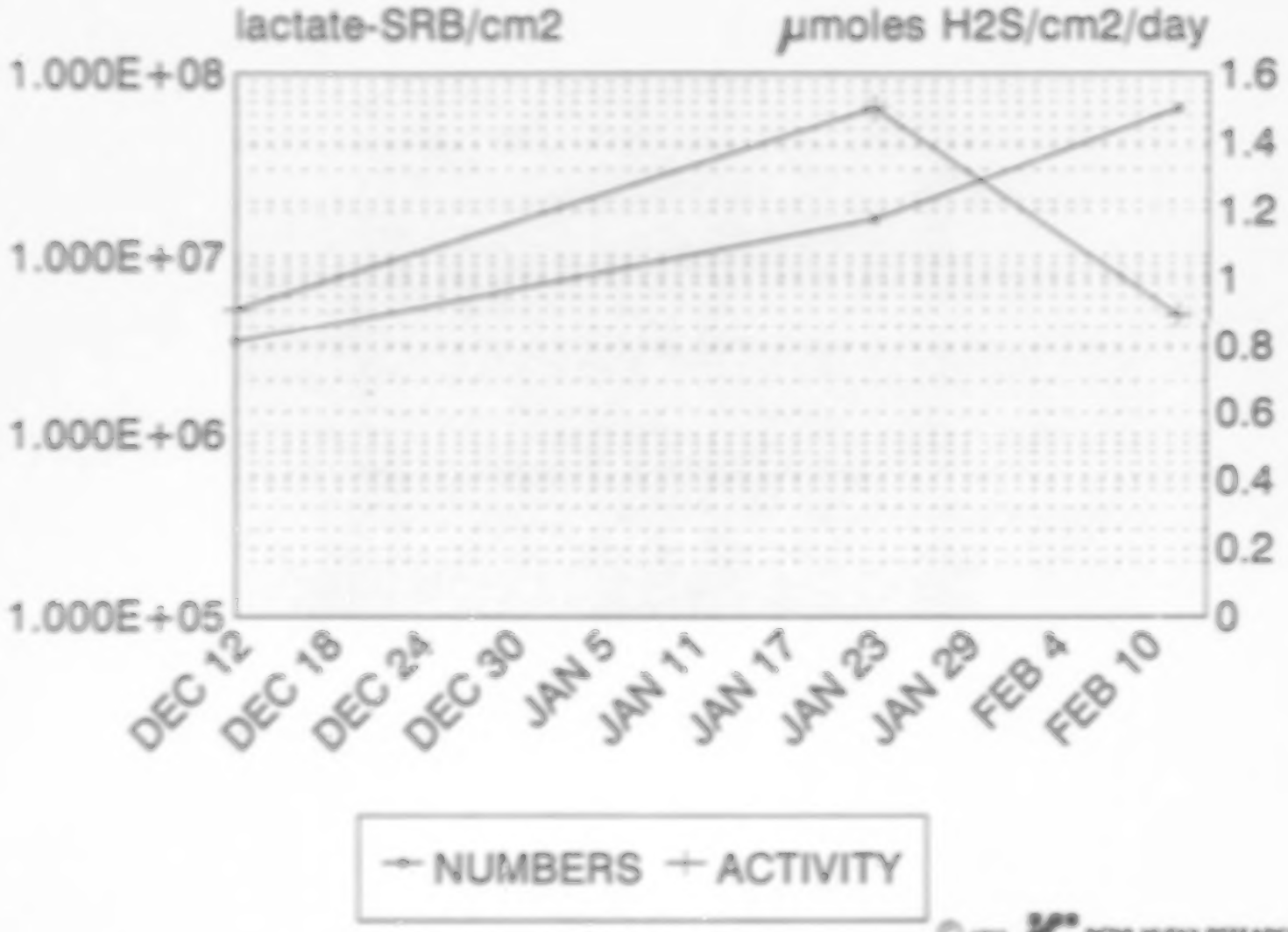

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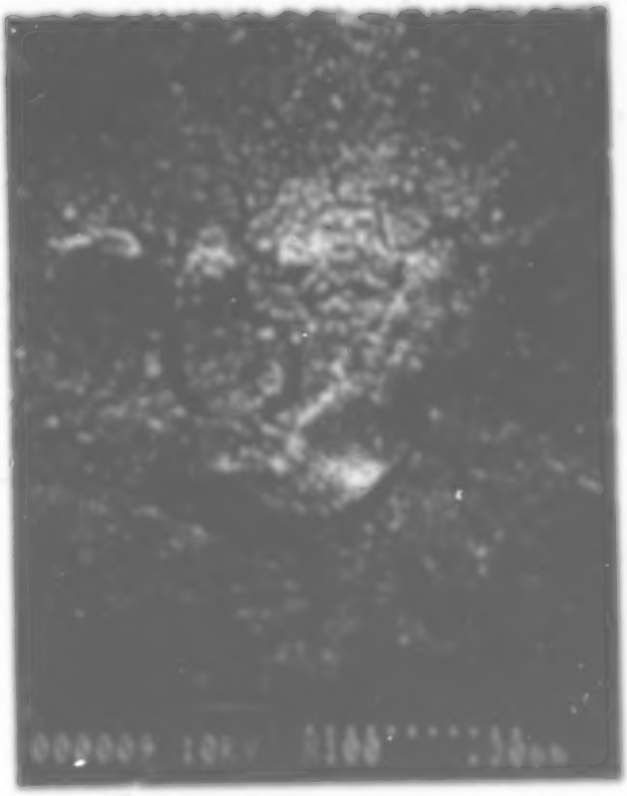
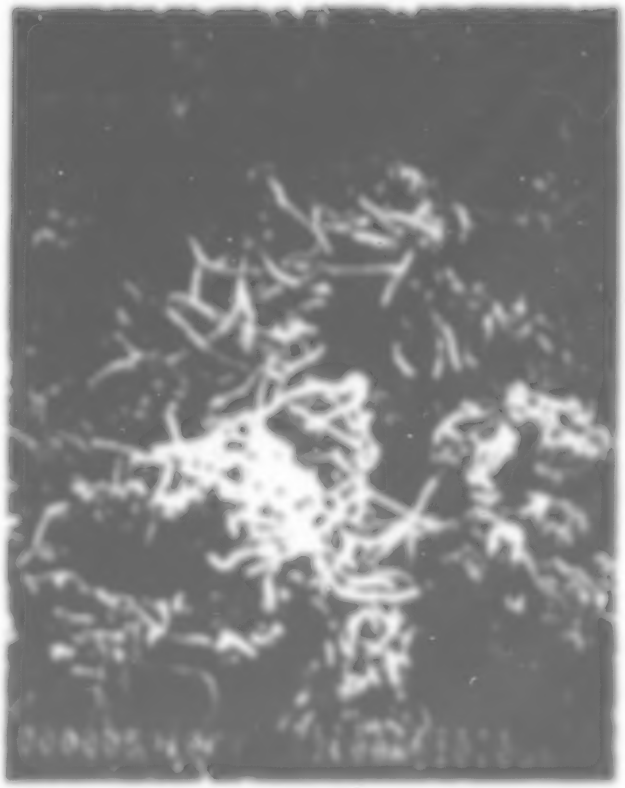
Figure 61: Scanning electron micrograph of surface deposits, line 2 control, showing areas of smooth, thin deposits and thicker, sometimes porous deposits typical of lines 2 to 5



© [illegible]

Figure 52: Scanning electron micrograph for biofilm, time 1 + nitrate. Coplaque cells were evident consistent with heavy fouling



© 1992 [illegible]

Figure 53: Energy dispersive x-ray analysis of biolitin, line 1 + nitrate showing the presence of calcium and iron but absence of sulfide

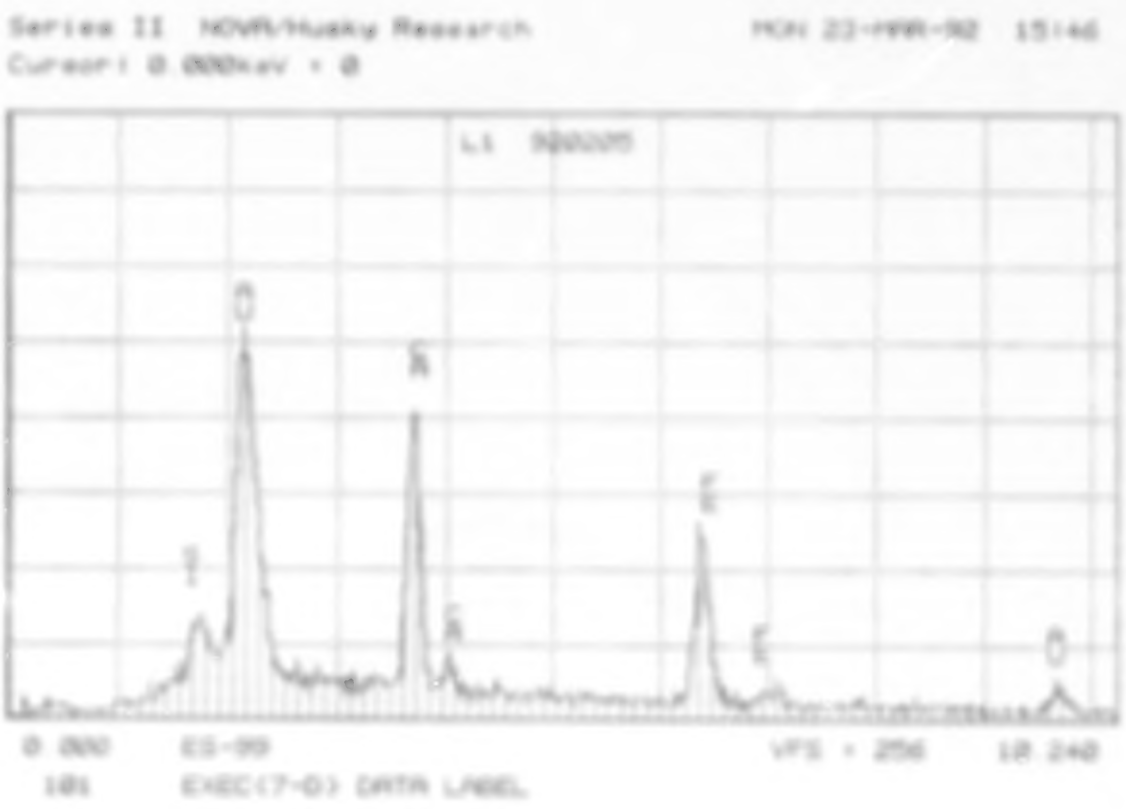


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Figure 54: Energy dispersive x-ray analysis of biofilm, line 3 showing the calcium iron and sulfide rich deposits typical of lines 2 to 5

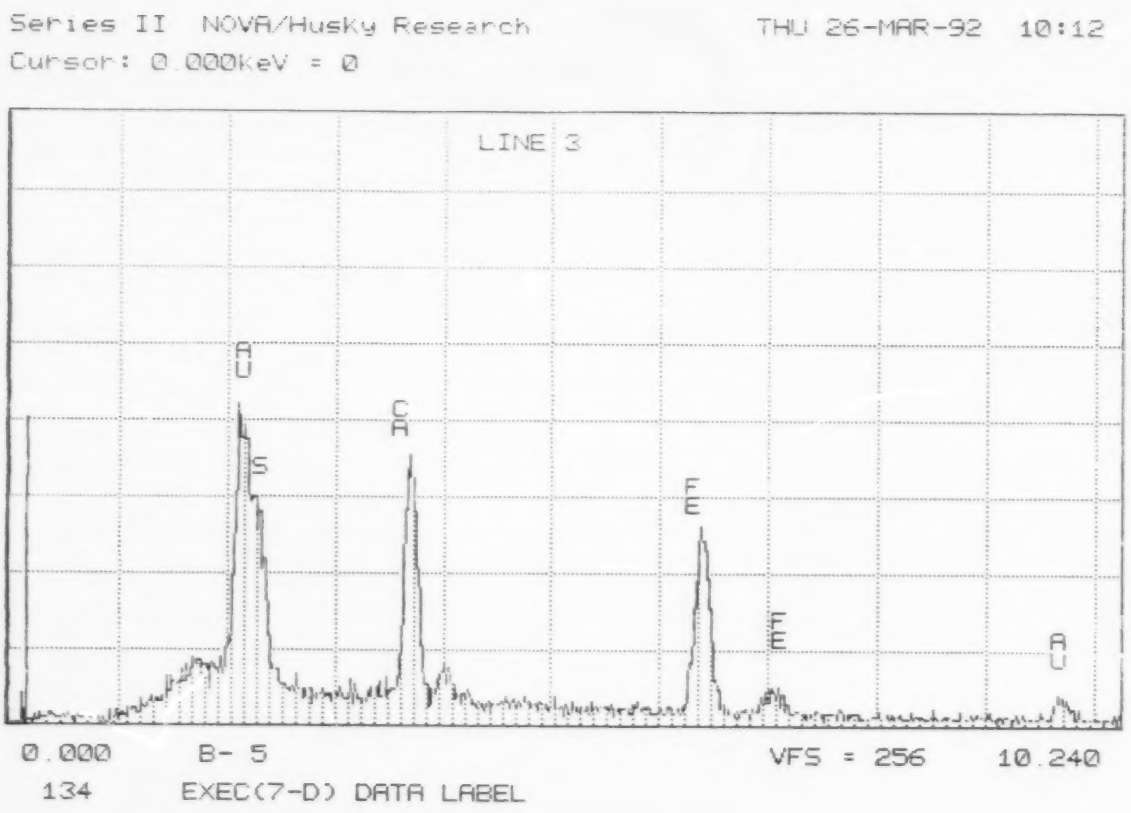

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Figure 55: Scanning electron micrograph of biofilm, line 4 + acetate/lactate showing the presence of lacy network of dehydrated polymer and organisms

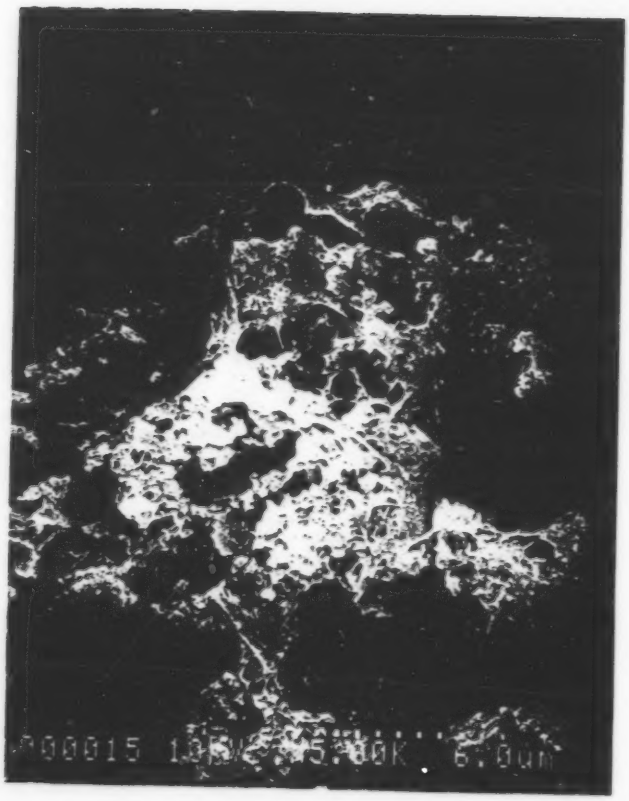

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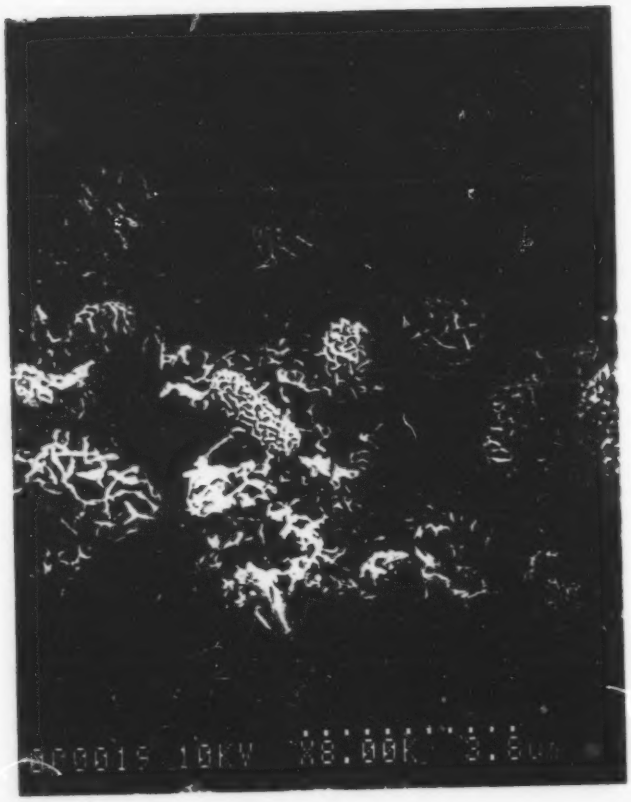
Figure 56: Scanning electron micrograph of distinctive mineralization, line 4 + acetate/lactate rich in iron sulfide



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APPENDIX A
Field Audit Data and Microbial Population Distributions for the Wainwright Waterflood

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MEDIAN VALUES

	APB FWKO	APB WP	SRB FWKO	SRB WP	SRB WP/FWKO	SO4 FWKO	SO4 WP
Unit #1	13000	13000	595	930000	1563.03	0.03	0.11
Unit #5	7200	13000	460	1700000	3695.65	0.03	0.06
Unit #6	1400	13000	2250	2250000	1000.00	0.03	0.03
Unit #14	1300	130000	530	2500000	4716.98	0.05	0.06
Unit #20	130	130	3900	250000	64.10	0.06	0.17
Unit #28	1300	15	320	6600	20.63	0.06	0.06
Truckpit	1310 *	11450	930000 *	2200000	2.37	0.15	0.17

*Upper Waterplant

AVERAGE VALUES

	pH FWKO	pH WP	pH ALL	Density (g/mL) FWKO	Density (g/mL) WP	Density (g/mL) ALL
Unit #1	6.78	6.88	6.83	1.03	1.02	1.03
Unit #5	6.78	6.80	6.79	1.04	1.04	1.04
Unit #6	6.78	6.85	6.82	1.03	1.03	1.03
Unit #14	6.99	6.93	6.96	1.05	1.02	1.03
Unit #20	6.64	6.55	6.59	1.04	1.04	1.04
Unit #28	6.70	6.69	6.70	1.04	1.04	1.04
Truckpit		6.75			1.06	

AVERAGE VALUES

	Resist (ohm-cm) FWKO	Resist (ohm-cm) WP	Resist (ohm-cm) ALL	Conduct (µs/cm) FWKO	Conduct (µs/cm) WP	Conduct (µs/cm) ALL
Unit #1	20.3	22.7	21.5	48513	46222	47300
Unit #5	16.5	16.1	16.3	65640	64075	64944
Unit #6	18.9	19.0	19.0	55267	54780	55011
Unit #14	14.3	34.8	25.1	75913	31322	52306
Unit #20	15.3	15.3	15.3	67289	68333	67811
Unit #28	15.3	14.6	14.9	68233	69511	68872
Truckpit		11.4			88622	

AVERAGE VALUES

	Oil&grease (mg/L) FWKO	Oil&grease (mg/L) WP	Oil&Grease (mg/L) ALL	Hardness (mg/L) FWKO	Hardness (mg/L) WP	Hardness (mg/L) ALL
Unit #1	3281	117	1606	4665	4173	4405
Unit #5	1795	181	1078	7221	6629	6958
Unit #6	183	39	107	5163	5059	5108
Unit #14	10020	45	4409	8815	3019	5747
Unit #20	490	59	274	14789	7448	11118
Unit #28	432	93	263	7426	7413	7419
Truckpit		40			11309	

AVERAGE VALUES

	Dis. solid (mg/L) FWKO	Dis. solid (mg/L) WP	Dis. solid (mg/L) ALL	Sus. solid (mg/L) FWKO	Sus. solid (mg/L) WP	Sus. solid (mg/L) ALL
Unit #1	36150	34478	35265	1586	86	792
Unit #5	54400	53000	53778	879	149	555
Unit #6	42522	42970	42758	58	38	47
Unit #14	65113	21889	42229	97	68	82
Unit #20	55789	55633	55711	173	81	127
Unit #28	58200	57967	58083	182	58	120
Truckpit		81880			327	

AVERAGE VALUES

	Oil freeSS (mg/L) FWKO	Oil freeSS (mg/L) WP	Oil freeSS (mg/L) ALL
Unit #1	65	48	56
Unit #5	149	40	101
Unit #6	21	24	23
Unit #14	73	25	48
Unit #20	35	46	40
Unit #28	26	27	26
Truckpit		123	

AVERAGE VALUES

	Sodium (mg/L) FWKO	Sodium (mg/L) WP	Sodium (mg/L) ALL	Calcium (mg/L) FWKO	Calcium (mg/L) WP	Calcium (mg/L) ALL
Unit #1	12469	11611	12015	943	919	930
Unit #5	18141	17758	17971	1623	1427	1536
Unit #6	15140	14616	14864	1148	1125	1136
Unit #14	22073	7276	14239	1921	667	1257
Unit #20	19604	18601	19103	1535	1670	1602
Unit #28	19420	19514	19467	1706	1716	1711
Truckpit		27617			2479	

AVERAGE VALUES

	Magnesium (mg/L) FWKO	Magnesium (mg/L) WP	Magnesium (mg/L) ALL	Iron (mg/L) FWKO	Iron (mg/L) WP	Iron (mg/L) ALL
Unit #1	499	457	477	8.89	31.09	20.64
Unit #5	772	747	761	10.92	9.52	10.30
Unit #6	559	548	553	7.48	26.35	17.41
Unit #14	979	329	635	20.00	8.01	13.65
Unit #20	769	797	783	43.85	8.10	25.98
Unit #28	770	762	766	5.88	6.68	6.28
Truckpit		1161			12.38	

AVERAGE VALUES

	Potassium (mg/L) FWKO	Potassium (mg/L) WP	Potassium (mg/L) ALL	Barium (mg/L) FWKO	Barium (mg/L) WP	Barium (mg/L) ALL
Unit #1	214	198	205	65.1	57.5	61.1
Unit #5	331	314	324	106.1	97.6	102.3
Unit #6	263	264	264	61.2	64.8	63.1
Unit #14	357	118	230	124.1	36.9	77.9
Unit #20	317	351	334	87.3	54.4	70.8
Unit #28	368	376	372	91.6	95.3	93.4
Truckpit		592			110.1	

AVERAGE VALUES

	Manganese (mg/L) FWKO	Manganese (mg/L) WP	Manganese (mg/L) ALL	Chloride (mg/L) FWKO	Chloride (mg/L) WP	Chloride (mg/L) ALL
Unit #1	0.23	0.42	0.33	21417	20670	21021
Unit #5	0.30	0.29	0.30	32889	32141	32556
Unit #6	0.31	0.39	0.35	27390	25739	26521
Unit #14	0.34	0.25	0.29	39283	13093	25418
Unit #20	0.72	0.36	0.54	33533	33567	33550
Unit #28	0.37	0.37	0.37	35303	34959	35131
Truckpit		0.58			49421	

AVERAGE VALUES

	Bicarb (mg/L) FWKO	Bicarb (mg/L) WP	Bicarb (mg/L) ALL	Sulphate (mg/L) FWKO	Sulphate (mg/L) WP	Sulphate (mg/L) ALL
Unit #1	527	528	528	0.4	6.9	3.9
Unit #5	483	494	488	0.2	1.5	0.8
Unit #6	591	580	585	0.5	5.3	3.1
Unit #14	339	367	354	0.1	5.5	4.7
Unit #20	502	437	469	129.7	163.3	149.9
Unit #28	540	544	542	0.4	1.1	0.9
Truckpit		484			1.0	

AVERAGE VALUES

	Fail freq.	Fail cost Total ($)	Iron FWKO	Iron WP (mg/l)	Iron ALL	Manganese FWKO	Manganese WP (mg/l)	Manganese ALL
Unit #1	6	10363.52	31.38	12.33	19.25	0.63	0.35	0.45
Unit #5	2	11111.14	14.60	11.78	12.82	0.36	0.29	0.32
Unit #6	3	2702.92	10.77	0.00	10.48	0.37	0.36	0.36
Unit #12	3	41077.60	0.00	12.69	0.00	0.00	0.29	0.00
Unit #13	3	1225.00	30.25	10.62	16.56	0.83	0.55	0.60
Unit #14	14	25308.72	37.31	28.30	30.75	0.58	0.33	0.38
Unit #20	44	151186.85	21.06	15.57	16.95	0.48	0.46	0.47
Unit #28	22	11654.26	13.40	10.07	10.91	0.45	0.55	0.52
Truckpit	4	5502.48	0.00	24.85	0.00	0.00	0.86	0.00

AVERAGE VALUES

	pH FWKO	pH WP	pH ALL	Scale Res FWKO	Scale Res WP (ppm)	Scale Res ALL
Unit #1	7.13	7.16	7.15	45	27	34
Unit #5	7.04	7.09	7.07	76	12	17
Unit #6	7.16	7.18	7.17	20	14	15
Unit #12	0.00	6.87	0.00	0	29	0
Unit #13	7.14	7.08	7.09	16	13	13
Unit #14	7.05	7.29	7.10	46	31	35
Unit #20	7.10	7.12	7.11	11	13	13
Unit #28	7.04	6.96	6.98	46	4	12
Truckpit	0.00	7.06	0.00	0	22	0

AVERAGE VALUES

	Inh. Res FWKO	Inh. Res WP (ppm)	Inh. Res ALL	Coup gen FWKO	Coup gen WP (mpy)	Coup gen ALL
Unit #1	24	42	42	2.8	0.1	0.8
Unit #5	24	50	50	3.3	0.4	1.0
Unit #6	56	154	152	-1.4	1.0	0.8
Unit #12	0	26	0	0.0	0.4	0.0
Unit #13	68	85	79	2.8	1.1	1.3
Unit #14	40	26	29	0.3	0.4	0.3
Unit #20	72	87	86	9.1	2.9	3.7
Unit #28		83	83	1.0	0.3	0.4
Truckpit	0	101	0	0.0	19.1	0.0

AVERAGE VALUES

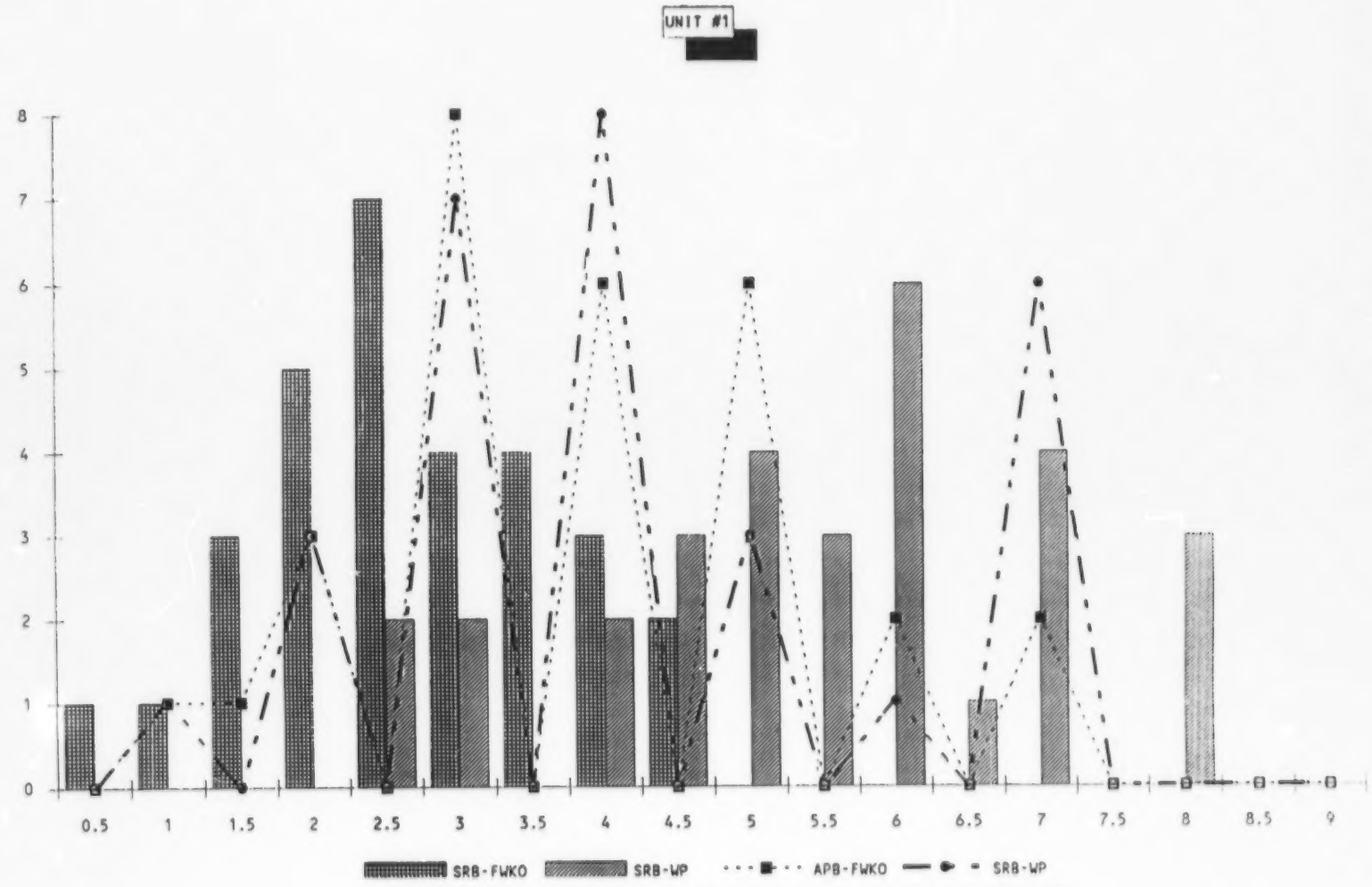
	Report P FWKO (mpy)	Report P WP	Report P ALL	Pot gen FWKO	Pot gen WP (mpy)	Pot gen ALL
Unit #1	12.6	1.3	4.3	7.9	0.1	2.7
Unit #5	5.5	9.0	8.2	0.0	2.1	1.8
Unit #6	0.0	12.6	12.2	0.0	0.2	0.2
Unit #12	0.0	1.3	0.0	0.0	0.3	0.0
Unit #13	2.0	13.8	9.9	0.0	7.6	5.8
Unit #14	5.0	5.8	5.7	0.1	1.1	0.8
Unit #20	3.9	2.8	3.0	0.1	0.2	0.2
Unit #28	0.0	0.4	0.3	1.0	-0.4	-0.1
Truckpit	0.0	61.7	0.0	0.0	0.5	0.0

AVERAGE VALUES

	Pot pit FWKO	Pot pit WP	Pot pit ALL	Sulphite FWKO	Sulphite WP (mg/l)	Sulphite ALL
Unit #1	125.8	1.8	43.1	6.0	4.9	4.9
Unit #5		22.9	22.9	5.4	4.8	4.8
Unit #6	0.1	3.5	2.2		7.0	7.0
Unit #12	0.0	7.9	0.0	0.0		0.0
Unit #13	1.0	67.1	41.3		9.5	9.5
Unit #14	2.6	24.3	17.0		12.1	12.1
Unit #20	0.5	0.8	0.7		3.6	3.6
Unit #28	7.3	-0.3	1.7		2.6	2.6
Truckpit	0.0	1.6	0.0	0.0	9.0	0.0

ReportP = estimated pitting from visual examination (mpy)
pot gen = potentiodyne general corrosion rate (mpy)
pot pit = potentiodyne pitting index
sulphite = residual sulphite from ammonium bisulfite oxygen scavenger addition

Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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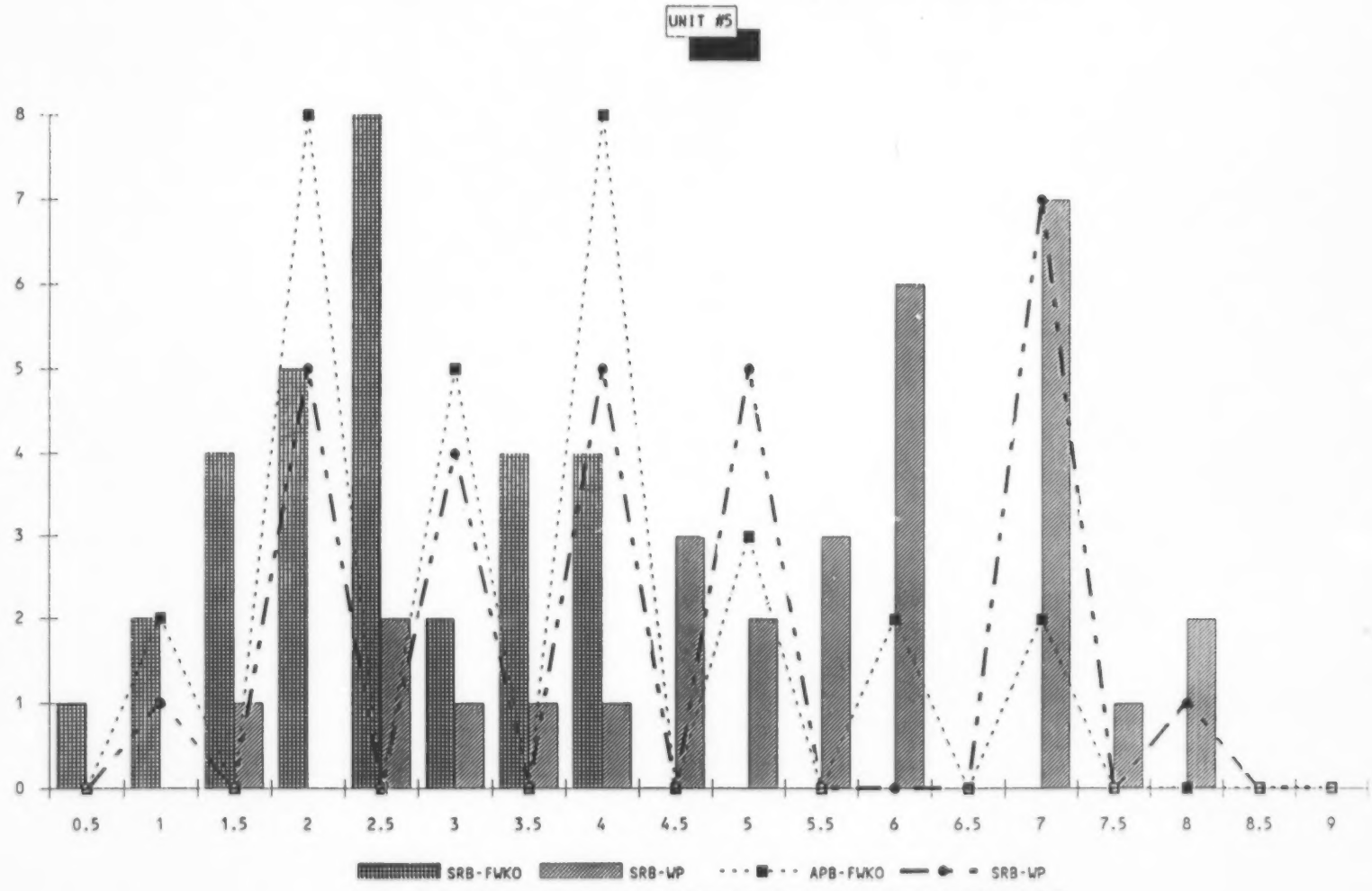
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

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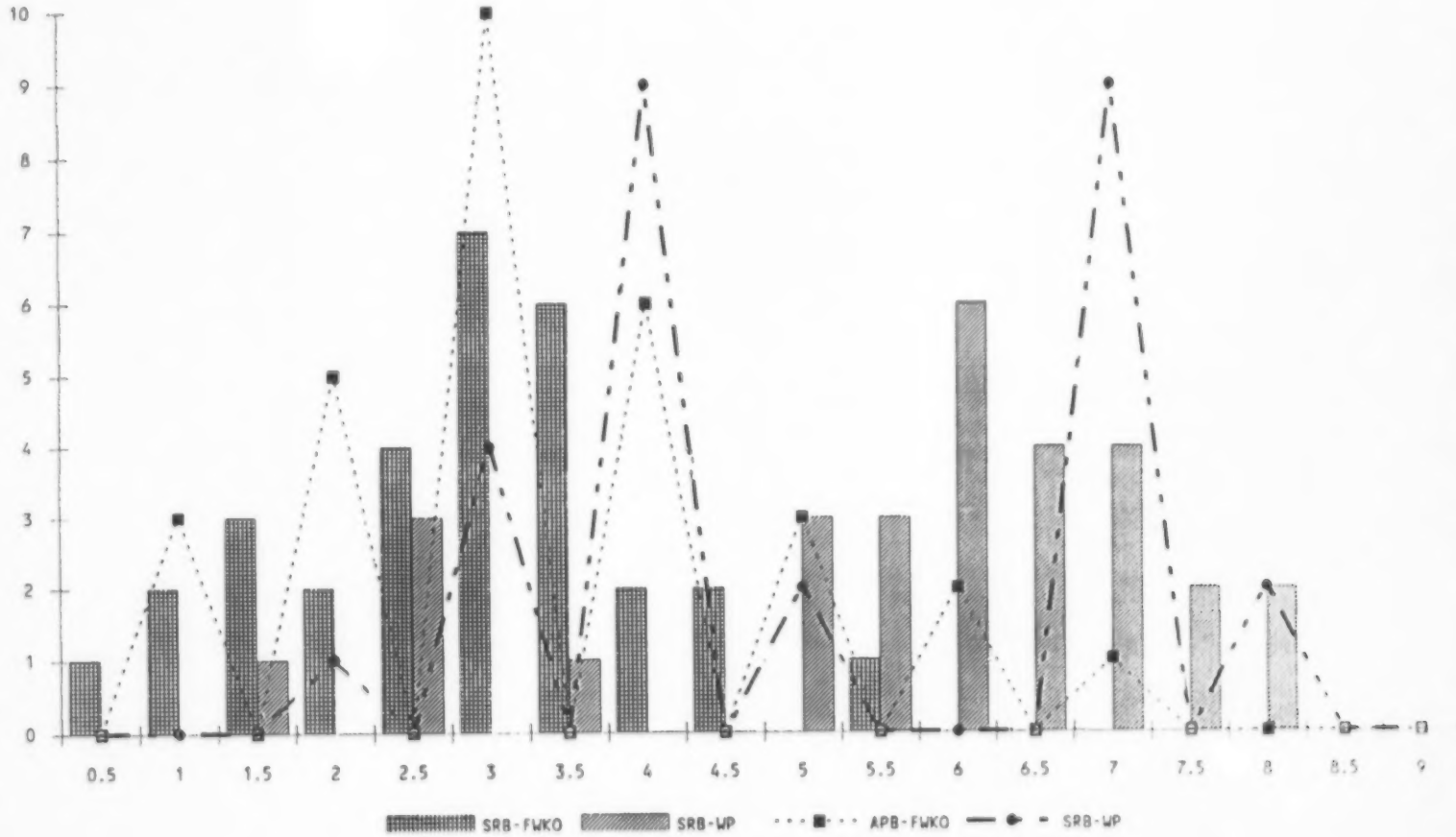
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit

UNIT #6 [redacted]



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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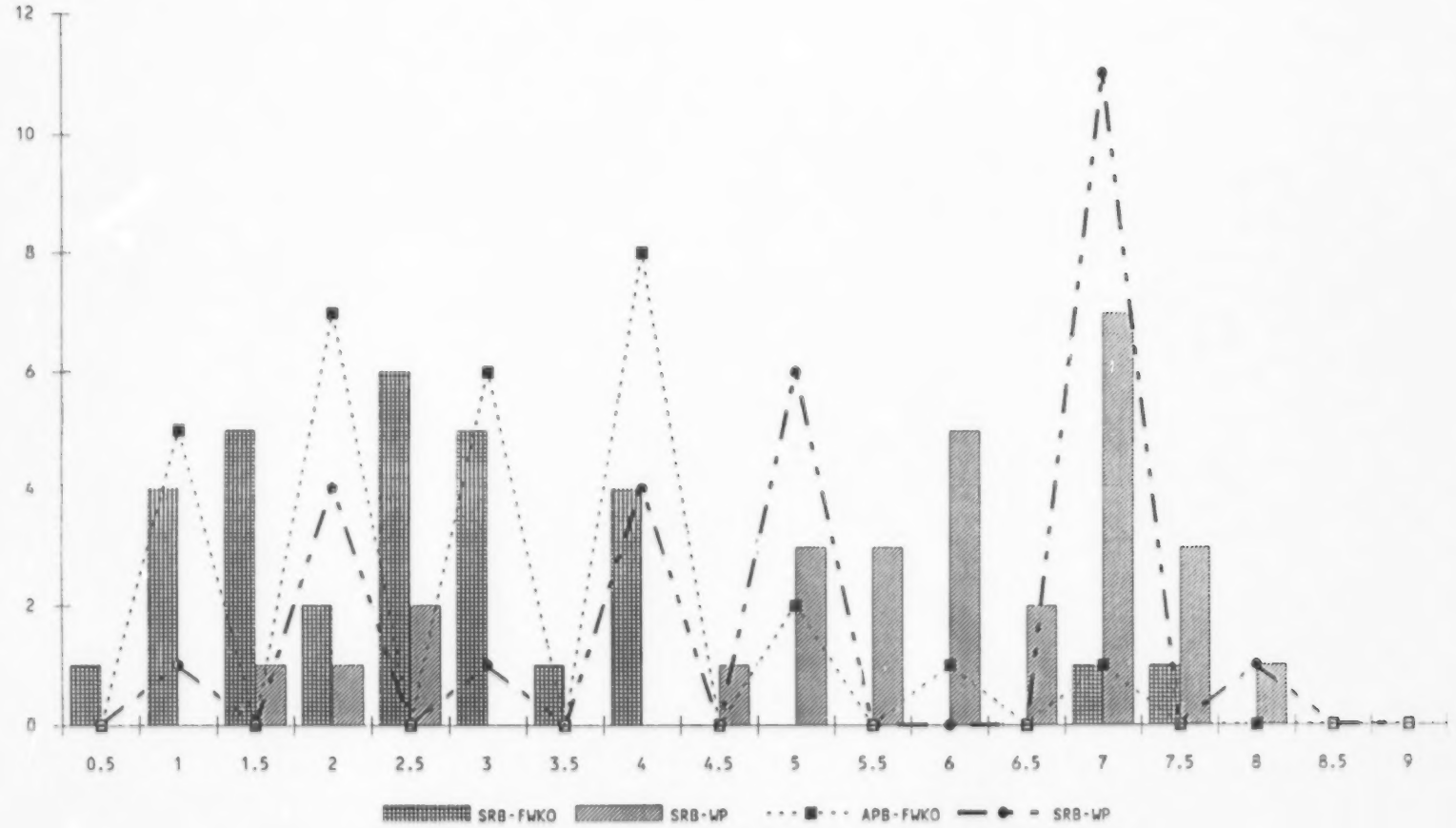
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit

UNIT #14 [redacted]



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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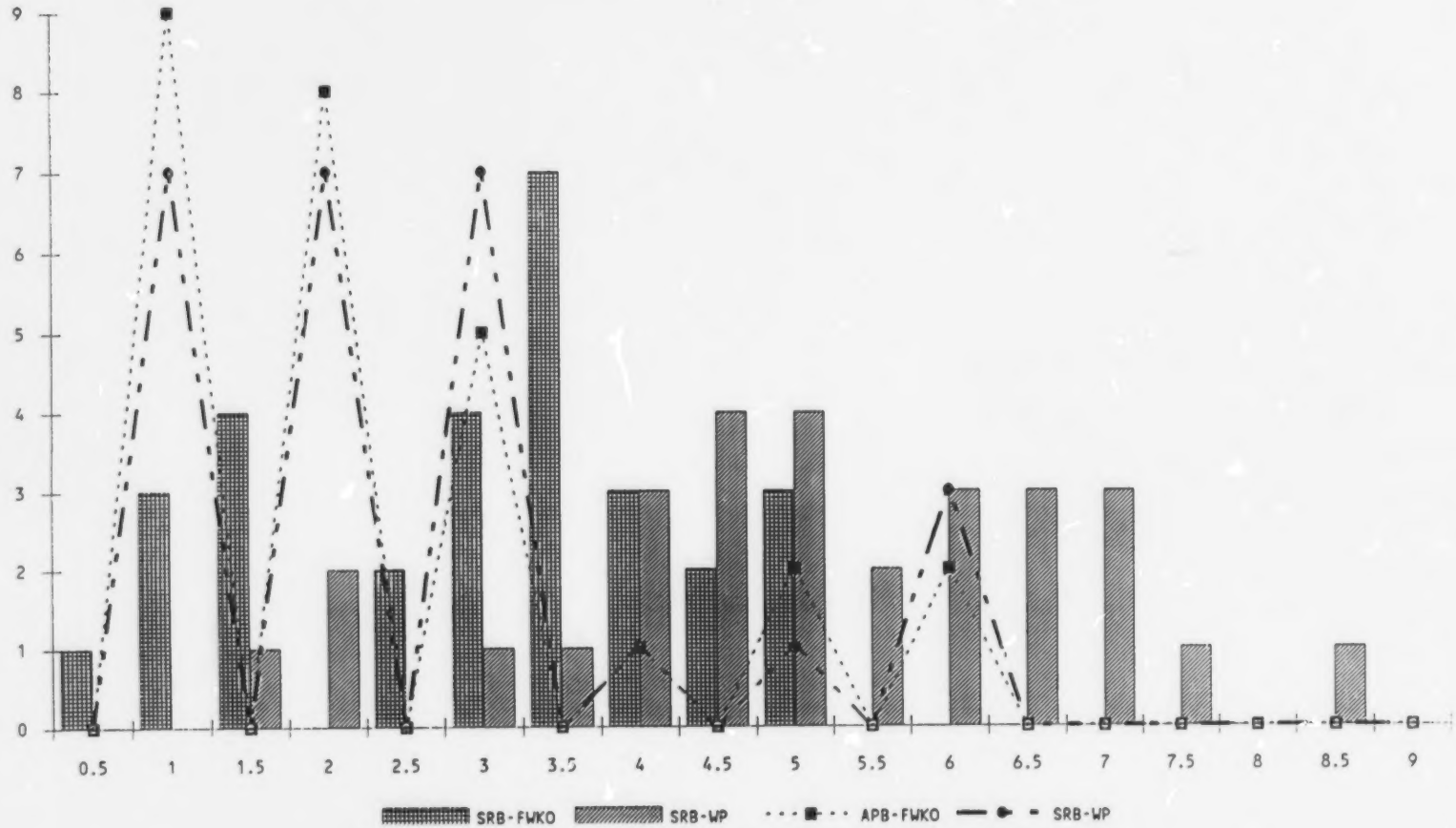
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit

UNIT #20 [redacted]



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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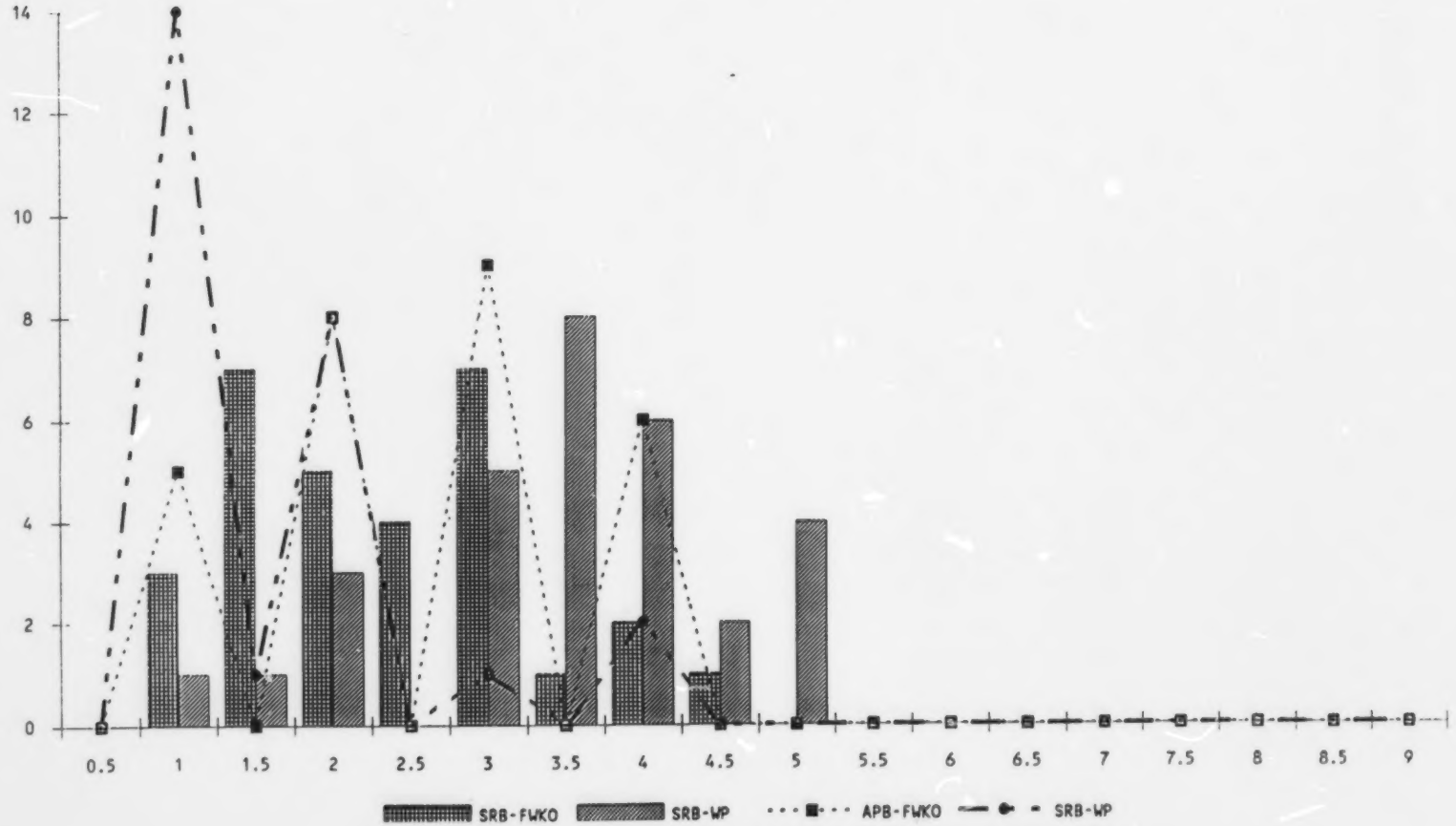
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit

UNIT #28 [redacted]



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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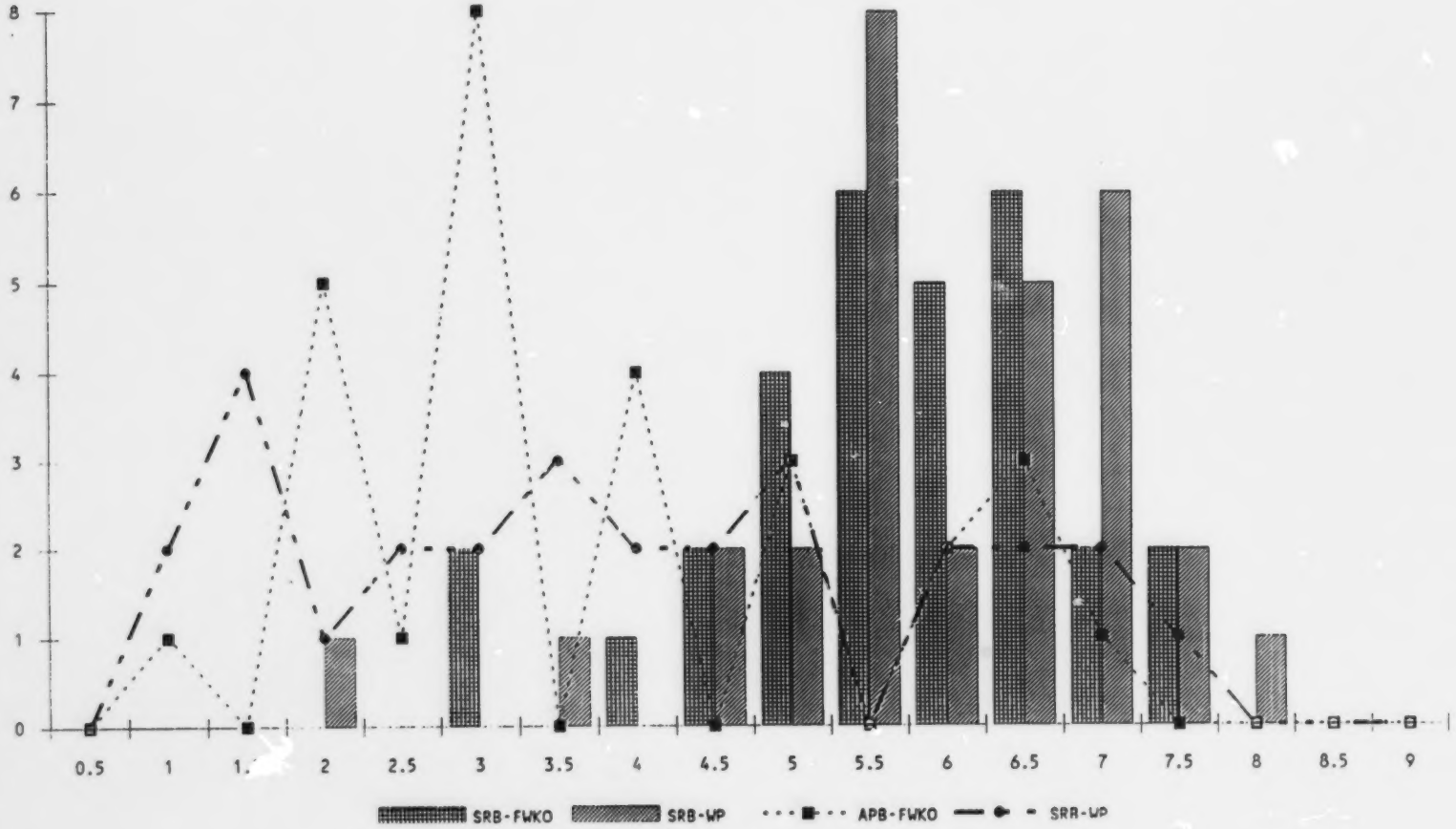
Distributions for Sulfate-Reducing Bacteria (SRB) and Acid-Producing Bacteria (APB) measurements in Units 1, 5, 6 and 4, Battery 20 and 28 and Truckpit

TRUCKPIT [redacted]



Frequency of Measurement is plotted against population density LOG (viable cells/cm^2) in each case

(N.B. zero readings for APB plots at 0.5, 1.5, 2.5, 3.5 etc. are an artifact of the assay procedure and plotting software)

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APPENDIX B

Growth Media

Growth Medium for Acetate Utilizing Bacteria	
SOLUTION 1	
NaCl	20.0 g
$MgCl_2 \cdot 6H_2O$	3.0 g
NH_4Cl	0.3 g
Na_2SO_4	4.0 g
KH_2PO_4	0.2 g
KCl	0.3 g
$CaCl_2 \cdot 2H_2O$	0.15 g
resasurin	10 ml (0.1 g/l)
distilled H_2O	960 ml

- autoclave & put in anaerobic chamber immediately following sterilization.
- add aliquots from solutions 2 through 7.
- final pH should be 7.0 - 7.5.

SOLUTION 2	
HCl	4.5 ml
$FeCl_2 \cdot 4H_2O$	1.5 g
H_3BO_3	0.060 g
$MnCl_2 \cdot 6H_2O$	0.10 g
$ZnCl_2$	0.07 g
$NiCl_2 \cdot 6H_2O$	0.025 g
$CuCl_2 \cdot 2H_2O$	0.015 g
$Na_2MoO_4 \cdot 2H_2O$	0.025 g
distilled H_2O	995 ml

- autoclave & put in anaerobic chamber.
- add 1 ml to 1 l solution 1.

SOLUTION 3 (selenite solution)	
$Na_2SeO_3 \cdot 5\ H_2O$	0.003 g
NaOH	0.005 g
distilled H_2O	1000 ml

- autoclave & put in anaerobic chamber.
- add 1 ml to 1 l solution 1.

SOLUTION 4	
$NaHCO_3$	8.4 g
distilled H_2O	100 ml

- saturate with CO_2 or N_2 gas for few minutes & filter sterilize.
- put in anaerobic chamber.
- add 30 ml per 1 l of solution 1.

SOLUTION 5	
$Na_2S \cdot 9\ H_2O$	1.2 g
distilled H_2O	10 ml

- distilled H_2O is freshly boiled.
- autoclave and immediately put in anaerobic chamber.
- add 1 ml to 1 l solution 1.

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SOLUTION 6 (growth factors)	
biotin	0.01 g
4 - aminobenzoic acid	0.04 g
thiamine hydrochloride	0.100 g
B_{12}	0.05 g
nicotinic acid	0.100 g
distilled H_2O	1000 ml

- filter sterilize and put in anaerobic chamber.
- add 1 ml to 1 l solution 1.

SOLUTION 7 (carbon sources)	
Na-acetate · $3H_2O$	20 g
distilled H_2O	100 ml

- autoclave & put in anaerobic chamber.
- add 10 ml to 1 l solution 1.

SODIUM DITHIONITE REDUCING AGENT	
$Na_2S_2O_4$	1.25 g
distilled H_2O	25 ml

- boil distilled H_2O, add $Na_2S_2O_4$ & filter sterilize.

NOTE: make just before use - an old solution loses reducing power
- can be stored @ 4°C for a few days for continued use.

APPENDIX C

Water Analyses

CHEMICAL & GEOLOGICAL LABORATORIES LTD.

WATER ANALYSIS

DATE REPORTED: January 24, 1992 LAB REPORT NO: C92-2718

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: December 13, 1991 ANALYST: P. Kelly

Lab Number	C2-2718-1	C92-2718-2	C92-2718-3	C92-2718-4	C92-2718-5
Sample ID	Line 1 ~~(Sulphate)~~ Nitrate	Line 2 ~~(Nitrate)~~ LAMINAR	Line 3 (Control)	Line 4 (acetate, Lactate)	Line 5 (Oxygen scavenger)
Sodium (mg/L)	22070	22160	21150	22440	21890
Potassium (mg/L)	407	407	391	407	454
Calcium (mg/L)	1956	1844	1916	1964	1924
Magnesium (mg/L)	1002	1026	977	977	1021
Iron (mg/L)	1.91	1.89	0.90	0.05	0.21
Barium (mg/L)	34.8	28.3	37.8	42.9	38.2
Bicarbonate (mg/L)					
Sulphate (mg/L)	19		16	29	23
Sulphide *	NIL	NIL	NIL	NIL	NIL
Nitrate as N (mg/L)		0.18	0.09		0.14
Total Kjeldahl N (mg/L)		72.0	73.5		72.0

(* Qualitative test only)

Insufficient sample for further analyses.

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CHEMICAL & GEOLOGICAL LABORATORIES LTD.

WATER ANALYSIS

DATE REPORTED: January 24, 1992 LAB REPORT NO: C92-2825

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: January 7, 1992 ANALYST: P. Kelly

DATE SAMPLED: December 22, 1991

Lab #	2825-1	2825-2	2825-3	2825-4	2825-5
Sample ID	Bio-Skid Line #1	Bio-Skid Line #2	Bio-Skid Line #3	Bio-Skid Line #4	Bio-Skid Line #5
Sodium (mg/L)	23720	23720	23900	23350	23900
Potassium (mg/L)	440	470	470	440	440
Calcium (mg/L)	3220	3150	3430	2650	2200
Magnesium (mg/L)	1550	1520	1090	1450	1380
Chloride (mg/L)	45500	45500	45250	45250	45500
Sulphate (mg/L)	31	23	16	25	33
Sulphide (mg/L)	2.60	2.65	2.55	2.90	2.95
Bicarbonate (mg/L)	488	519	458	519	519
Iron (mg/L)	4.60	3.59	2.06	0.04	2.37
Nitrate-N (mg/L)	4.50	0.75	0.18	<0.01	0.29
Total Kjeldahl N (mg/L)		69.8			

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CHEMICAL & GEOLOGICAL LABORATORIES LTD.

WATER ANALYSIS

DATE REPORTED: January 24, 1992 LAB REPORT NO: C92-2830

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: January 8, 1992 ANALYST: P. Kelly

DATE SAMPLED: January 7, 1992

Lab #	2830-1	2830-2	2830-3	2830-4	2830-5
Sample ID	Line #1	Line #2	Line #3	Line #4	Line #5
Sodium (mg/L)	21875	21695	21875	22060	21695
Potassium (mg/L)	405	375	405	405	375
Calcium (mg/L)	2460	2190	2020	2220	1880
Magnesium (mg/L)	1100	1020	973	1040	909
Chloride (mg/L)	41050	41000	41000	41250	41250
Sulphate (mg/L)	5	16	3	5	43
Sulphide (mg/L)					
Bicarbonate (mg/L)	702	671	641	732	610
Iron (mg/L)	1.15	2.41	14.7	2.15	3.60
Nitrate-N (mg/L)	8.50	0.05	0.06	0.05	0.05
Total Kjeldahl N (mg/L)		66.0			

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CHEMICAL & GEOLOGICAL LABORATORIES LTD.

WATER ANALYSIS

DATE REPORTED: January 24, 1992

LAB REPORT NO: C92-2916

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: January 14, 1992

ANALYST: P. Kelly

DATE SAMPLED: January 14, 1992

Lab #	2916-1	2916-2	2916-3	2916-4	2916-5
Sample ID	Line #1	Line #2	Line #3	Line #4	Line #5
Sulphide (mg/L)	0.75	0.90	0.85	0.80	0.90

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CHEMICAL & GEOLOGICAL LABORATORIES LTD.

WATER ANALYSIS

DATE REPORTED: February 3, 1992 LAB REPORT NO: C92-2967

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: January 21, 1992 ANALYST: P. Kelly

DATE SAMPLED: January 21, 1992

Lab #	2967-1	2967-2	2967-3	2967-4	2967-5
Sample ID	Bio-Skid Line #1	Bio-Skid Line #2	Bio-Skid Line #3	Bio-Skid Line #4	Bio-Skid Line #5
Sodium (mg/L)	22430	21875	21325	21325	21325
Potassium (mg/L)	420	405	420	420	420
Calcium (mg/L)	1954	1986	2002	1930	2082
Magnesium (mg/L)	1073	1078	1049	1131	1044
Chloride (mg/L)	41350	41300	41500	41250	41500
Sulphate (mg/L)	18	20	16	3	3
Sulphide (mg/L)	2.65	3.45	2.70	2.85	2.65
Bicarbonate (mg/L)	641	641	641	671	665
Iron (mg/L)	4.93	29.5	5.04	5.07	5.12
Nitrate-N (mg/L)	11.45	0.31	0.10	0.09	0.09
Total Kjeldahl N (mg/L)		82.			

SIGNATURE OF SUPERVISOR Ph Kelly

CHEMICAL & GEOLOGICAL LABORATORIES INC.

WATER ANALYSIS

DATE REPORTED: February 21, 1992

LAB REPORT NO: C92-3094

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: February 5, 1992

ANALYST: P. Kelly

DATE SAMPLED: February 5, 1992

Lab Number	C2-2718-1	C92-2718-2	C92-2718-3
Sample ID	Bioskid Line #1	Bioskid Line #2	Bioskid Line #3
Sodium (mg/L)	21875	21695	22245
Potassium (mg/L)	405	405	420
Calcium (mg/L)	1994	1962	2002
Magnesium (mg/L)	1025	1073	1068
Chloride (mg/L)	42000	40950	41050
Iron (mg/L)	31.5	52.5	14.7
Bicarbonate (mg/L)	702	732	763
Sulphate (mg/L)	25	26	8
Sulphide (mg/L)	0.65	11.45	1.15
Nitrate as N (mg/L)	32.9	32.9	3.24
Total Kjeldahl N (mg/L)	74.1	54.1	

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CHEMICAL & GEOLOGICAL LABORATORIES INC.

WATER ANALYSIS

DATE REPORTED: February 21, 1992 LAB REPORT NO: C92-3184

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: February 12, 1991 ANALYST: P. Kelly

DATE SAMPLED: February 12, 1992

Lab Number	C2-2718-1	C92-2718-2
Sample ID	Bioskid Line #4	Bioskid Line #5
Sodium (mg/L)	22795	23165
Potassium (mg/L)	425	435
Calcium (mg/L)	1962	2002
Magnesium (mg/L)	1044	995
Chloride (mg/L)	41000	40250
Iron (mg/L)	5.61	5.20
Bicarbonate (mg/L)	854	702
Sulphate (mg/L)	16	5
Sulphide (mg/L)	3.35	3.30
Nitrate as N (mg/L)	0.09	7.7
Total Kjeldahl N (mg/L)		

SIGNATURE OF SUPERVIROR _____

CHEMICAL & GEOLOGICAL LABORATORIES INC.

WATER ANALYSIS

DATE REPORTED: March 6, 1992

LAB REPORT NO: C92-3231

NOVA HUSKY RESEARCH CORPORATION

DATE RECEIVED: February 19, 1992

DATE SAMPLED: February 18, 1992

ANALYST: P. Kelly

Lab #	3231-1	3231-2	3231-3	3231-4	3231-5
Sample ID	Bio-Skid Line #1	Bio-Skid Line #2	Bio-Skid Line #3	Bio-Skid Line #4	Bio-Skid Line #5
Sodium (mg/L)	21140	21140	21695	21875	21875
Potassium (mg/L)	440	440	440	440	440
Calcium (mg/L)	1914	1890	1962	1962	1882
Magnesium (mg/L)	1025	1039	1044	995	1044
Chloride (mg/L)	41500	41000	41000	41250	41500
Sulphate (mg/L)	18	40	28	21	18
Sulphide (mg/L)	0.67	0.60	0.27	0.31	0.37
Bicarbonate (mg/L)	488	604	671	702	610
Iron (mg/L)	5.38	22.6	12.0	9.59	10.4
Nitrate-N (mg/L)	0.07	0.10	0.13	0.07	0.13
Total Kjeldahl N (mg/L)	70.0	72.7			

SIGNATURE OF SUPERVISOR